CANADIAN JOURNAL OF RESEARCH

VOLUME 15 OCTOBER, 1937 NUMBER 10

CONTENTS

SEC. A.—PHYSICAL SCIENCES

Page

The Spectrum of α-Lyrae—*J. D. Babbitt* - - - - - - - 161

SEC. B—CHEMICAL SCIENCES

The Oxidation of Methane at High Pressures. II. Experiments with Various Mixtures of Viking Natural Gas and Air —*E. H. Boomer and V. Thomas* - - - - - - - - 401

The Oxidation of Methane at High Pressures. III. Experiments using Pure Methane and Principally Copper as Catalyst —*E. H. Boomer and V. Thomas* - - - - - - - - 414

Derivatives of Substituted Succinic Acids. III. The Action of Alkaline Sodium Hypobromite on Phenylsuccinamide and $\alpha\alpha'$-Dimethylsuccinamide—*John A. McRae, Arthur W. Weston, and Charles F. Hubbs* - - - - - - - - - 434

The Catalytic Dehydration of Ethyl Alcohol by Alumina. II.— *W. A. Alexander, W. R. Horn, and L. A. Munro* - - - - - 438

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

Publications and Subscriptions

The Canadian Journal of Research is issued monthly in four sections, as follows;

A. Physical Sciences
B. Chemical Sciences
C. Botanical Sciences
D. Zoological Sciences

For the present, Sections A and B are issued under a single cover, as also are Sections C and D, with separate pagination of the four sections, to permit separate binding, if desired.

Subscription rates, postage paid to any part of the world (effective 1 April, 1939), are as follows:

	Annual	*Single Copy*
A and B	$ 2.50	$ 0.50
C and D	2.50	0.50
Four sections, complete	4.00	—

The Canadian Journal of Research is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

National Research Council, Ottawa, Canada.

Reprinted in entirety by photo-offset from the original issue.

Library

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 15, SEC. A. OCTOBER, 1937 NUMBER 10

THE SPECTRUM OF α-LYRAE[1]

BY J. D. BABBITT[2]

Abstract

Results are given of the measurement of spectrograms of the star α-Lyrae taken at the Dominion Astrophysical Observatory, Victoria, B.C. One hundred and fifty-six lines were found in the spectrum and 147 of these were identified. Microphotometer tracings of the Balmer series and of the stronger metallic lines were measured and the profiles were plotted. The total absorptions were obtained from the profiles and compared with previous measurements.

Introduction

A great advance has been made, both theoretically and observationally, in the study of the profiles of stellar absorption lines since Schwarzschild first investigated the H and K lines of ionized calcium in the solar spectrum. So successful has been the attack on this problem during recent years that this method of approach has now become one of the most powerful means of investigating the atmospheres of the stars. When the problem of the formation of absorption lines in a stellar atmosphere has been fully solved and it is possible to obtain theoretical profiles, which give a satisfactory explanation of the observed lines, then shall there be a method whereby first-hand information of such properties of stellar atmospheres as temperature, pressure, and composition can be obtained. So far, however, theory has been unable to produce an adequate explanation of the observed shapes of absorption lines and much work remains to be done on this subject. As a result of this failure of theory to produce a formula capable of satisfying observation, most of the work on line profiles has been concentrated on the study of total absorptions or equivalent widths. This has already produced very important results and should also produce, in the future, information of ever increasing value as clearer and better knowledge of these absorption lines is obtained.

Most of this work has been carried out on the Fraunhofer lines in the solar spectrum because there the intensity is very much greater than in the stars. It is important, however, that corresponding studies be undertaken on stellar spectra. Prof. H. H. Plaskett, of the University Observatory, Oxford, was kind enough to place at the author's disposal some spectrograms of the star α-Lyrae which he had taken at the Dominion Observatory, Victoria, Canada. During the exposure of these plates a neutral tint wedge was placed over the slit of the spectrograph, and the variation in intensity so obtained could be used

[1] *Manuscript received August 18, 1937.*
Contribution from the Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada.

[2] *Physicist, National Research Laboratories, Ottawa.*

as a means of calibrating the plate for photometric measurement. The present investigation was undertaken with the idea of measuring these plates and determining photometrically the profiles of the Balmer lines and of the stronger metallic lines in the spectrum; with these data it was hoped to test theoretical interpretations of the observed profiles with a vew to determining, among other things, the relative abundance of hydrogen to the metals on this star. Unfortunately, however, the author left Oxford before the latter part of the investigation could be completed, and the observational data are given in this paper that they may be used in future investigations.

In this paper the spectrograms have first been measured and the identity of as many of the lines as possible was determined. The profiles of the stronger lines were obtained and the total absorptions were measured from these profiles.

Wave-lengths and Identifications

Measurement of the Plates

The plates were measured on the Hilger measuring machine of the University Observatory, Oxford. Each spectrum was measured in the direct and reversed position, four different settings of the instrument being made for each measurement, and the mean of the two measurements was taken as the final reading for the line. The spectra were so broad that care had to be taken that no errors were introduced into the measurements by the curvature in the lines. Where possible all the lines were measured at the same position, but in some cases, owing to the variation in the intensity caused by the wedge, all the lines were not visible at the same wedge height, so that this procedure was impossible. Here the plates were measured in two sections, all the lines in each section being measured at the same height and the measurements from the two sections being then correlated so as to give one consistent set of readings, which was reduced as a whole. One plate (W445) was measured by Prof. H. H. Plaskett as well as by the author, in order to have one independent set of measurements which would eliminate the possibility of a personal error.

The reduction from millimetres to Angstrom units was carried out by means of a Hartmann formula, each set of measurements being reduced separately. By means of three stellar lines of which the identity was certain (Balmer lines were used where possible) the constants of the formula were determined for each plate, and, the wave-lengths having been calculated using these constants, most of the stronger metallic lines were easily identified. A number of these lines, chosen both for their intensity and sharpness in the spectra and for the absence of all possible blends, were then used to draw the curve of errors for the Hartmann formula, and from this curve the residual (O-C) was found for each individual wave-length. This residual was added to the wave-length computed by means of the formula, the result being the observed wave-length of the line. The standards used in these reductions are shown in Table I with an asterisk.

The mean of the wave-lengths computed from the plates (both values of the plate, which was measured twice, being used) is given as the final observed wave-length. In the reductions all wave-lengths were carried to the third decimal place, but in the mean value the third figure (and in some places the second) has been dropped as the accuracy did not warrant it. In measuring the plates all lines down to the absolute limit of visibility were measured, *i.e.*, everything on the plate that even remotely resembled a line, as it was assumed that lines due to spurious arrangements of silver grains would appear on only one plate. In the final list it was necessary to reject several as not representing actual stellar absorption lines. In rejecting these lines the following arbitrary criteria were used: All lines of wave-length shorter than 3800 Å were retained, as only one plate reached this region and it was impossible to distinguish between true and spurious lines. Between λ3800 and λ3900 Å all lines were rejected which were not registered on at least two plates, and above 3900 Å no line was retained unless it had been measured on three separate plates. In this way some real lines were almost certainly lost, but the loss of these lines is more than compensated for by the fact that there is little doubt that the lines finally retained are genuine.

Table of Wave-lengths

The wave-lengths finally determined are given in Table I. The second column contains the estimated intensity of the lines. These intensities are given in a purely arbitrary scale which has roughly the following value: The

TABLE I

Stellar λ, Å	Estimated intensity	Element	Lab. wave-length	Temperature class	E.P., volts
3679.4	2	H_τ	79.36		10.16
3683.1	*d* 1	H_σ	82.81		10.16
*3685.1	1.5	Ti II	85.197	IV	0.605
3686.7	2	H_ρ	86.83		10.16
3691.3	2	H_π	91.56		10.16
3697.3	2.5	H_ω	97.15		10.16
3703.8	2.5	H_ξ	03.86		10.16
3706.0	1.5	Ca II	06.02	V	3.110
		Ti II	06.22		
3709.2	0.3	Fe I	09.25	II	0.911
3711.8	*d* 5	H_ν	11.97		10.16
*3719.9	0.5	Fe I	19.938	I	0.000
3721.9	3.5	H_μ	21.94		10.16
3727.6	0.5	Fe I	27.62	II	0.954
3734.6	4	H_λ	34.37		10.16
3737.0	1	Ca II	36.90	V	3.137
		Fe I	37.14	I	0.051
3740.1	0.3				
*3741.8	1.5	Ti II	41.633	V	1.575
3743.4	0.4				
*3745.6	1	Fe I	45.56	I	0.087
		Fe I	45.90	I	0.121
3750.1	5	H_κ	50.15		10.16
*3758.2	*d* 0.5	Fe I	58.234	II	0.954
*3759.3	0.8	Ti II	59.294	IV	0.605
*3761.4	0.8	Ti II	61.322	IV	0.571

TABLE I—*Continued*

Stellar λ, Å	Estimated intensity	Element	Lab. wave-length	Temperature class	E.P., volts
3763.7	0.4	Fe I	63.79	II	0.986
3765.6	*d* 0.3	Fe I	65.54	IV	
3767.1	*d* 0.3	Fe I	67.19	II	1.007
3770.3	7	H_ι	70.63		10.16
3783.3	0.3				
3797.9	8	H_θ	97.90		10.16
*3815.93	0.5	Fe I	15.844	II	1.478
3820.42	0.7	Fe I	20.43	II	0.855
3824.40	0.4	Fe I	24.44	I A	0.000
*3825.88	0.7	Fe I	25.886	II	0.911
3827.77	0.4	Fe I	27.83	II	1.551
*3829.33	0.7	Mg I	29.36	II	2.697
*3832.29	0.7	Mg I	32.31	II	2.700
3835.40	8	H_η	35.39		10.16
*3838.29	0.9	Mg I	38.29	II	2.705
3843.31	0.3	Fe I	43.26	IV	
3849.93	0.3	Fe I	49.97	II	1.007
3853.63	0.3	Si II	53.68		6.827
3856.09	1	Si II	56.022		6.829
		Fe I	56.37	I A	0.051
3858.10	0.3				
3859.95	0.8	Fe I	59.91	I	0.000
3862.62	1	Si II	62.60		6.827
3865.56	0.4	Cr II	65.65		
		Fe I	65.53	II	1.007
3872.54	0.3	Fe I	72.51	II	0.986
3878.48	0.3	Fe I	78.02	II	0.954
		Fe I	78.58	II	0.087
		Fe I	78.66		2.443
*3889.05	10	H_ζ	89.052		10.16
3900.60	1	Ti II	00.54	V	1.126
3902.99	0.4	Fe I	02.95	II	1.551
3905.60	0.6	Si I	05.53		1.900
		Cr II	05.66		
*3913.47	1.1	Ti II	13.460	V	1.111
3920.55	0.3	Fe I	20.26	I	0.121
3922.84	0.4	Fe I	22.92	I	0.051
3927.94	0.3	Fe I	27.92	I	0.110
3930.30	0.5	Fe I	30.30	I	0.087
3931.97	0.3	Ti II	32.01		1.126
*3933.67	8	Ca II	33.664	II	0.000
3943.98	0.8	Al I	44.03		0.000
3956.53	0.3	Fe I	56.46	IV	
		Fe I	56.68	III	2.681
3961.51	0.5	Al I	61.54		0.014
*3968.46	5	Ca II	68.470	II	0.000
*3970.08	7	H_ϵ	70.075		10.16
4005.29	0.4	Fe I	05.25	II	1.551
*4012.38	0.6	Ti II	12.37	V	0.571
		Cr II	12.52		
4024.61	0.4				
4028.38	0.4	Ti II	28.33	V	1.884
*4045.81	1.8	Fe I	45.822	II	1.478
4053.90	0.4	Ti II	53.81	V	1.885
*4063.58	1.1	Fe I	63.604	II	1.551
4067.00	0.3	Fe I	66.98	III	
		Fe I	67.28	III	
*4071.74	0.9	Fe I	71.748	II	1.601
*4077.71	0.9	Sr II	77.71	II	0.000
*4101.74	10	H_δ	01.738		10.16
4122.71	0.3	Fe II	22.67		2.572

TABLE I—*Continued*

Stellar λ, Å	Estimated intensity	Element	Lab. wave-length	Temperature class	E.P., volts
*4128.04	1.0	Si II	28.051		9.794
*4130.85	0.9	Si II	30.876		9.796
4131.98	0.4	Fe I	32.06	II	1.601
4143.82	0.7	Fe I	43.42	III	
		Fe I	43.87	I	1.551
*4163.64	0.8	Ti II	63.647	V	2.579
4167.30	0.4	Mg I	67.39	III	4.327
*4171.90	0.6	Ti II	71.904	V	2.586
4173.44	1.0	Ti II	73.54	V	1.079
		Fe II	73.47		2.572
4177.70	0.4				
*4178.84	0.9	Fe II	78.868		2.572
4181.78	0.3	Fe I	81.76	III	
4187.16	*d* 0.3	Fe I	87.05	III	2.439
4198.95	*d* 0.4	Fe I	98.31	III	2.389
		Fe I	99.10	III	
4202.08	0.6	Fe I	02.03	I	1.478
4215.48	0.6	Sr II	15.52	II	0.000
4226.73	0.9	Ca I	26.73	I	0.000
4233.17	1.6	Fe II	33.16		2.572
4235.97	*d* 0.4	Fe I	35.95	III	2.415
4242.31	0.6	Cr II	42.35		3.854
4246.80	0.7	Sc II	46.83	III	0.314
†4250.10	0.4	Fe I	50.13	III	2.458
†4250.83	0.4	Fe I	50.79	II	1.551
4254.38	0.4	Cr I	54.34	II	0.000
4258.21	0.3	Fe II	58.16		2.693
4260.43	0.7	Fe I	60.49	III	2.389
4262.00	0.4	Cr II	61.90		3.848
4271.75	0.8	Fe I	71.17	III	2.439
		Fe I	71.76	II	1.478
4273.26	0.4	Fe II	73.31		2.693
4290.17	0.8	Ti II	90.22	V	1.160
4291.77	0.3				
4294.09	1	Ti II	94.10	V	1.079
		Fe I	94.13	II	1.478
4296.56	0.6	Fe II	96.56		2.693
*4300.06	1	Ti II	00.052	V	1.175
4301.89	0.4	Ti II	01.93	V	1.156
4303.17	0.7	Fe II	03.18		2.693
4307.87	1.2	Ti II	07.86	V	1.160
		Fe I	07.91	II	1.551
4312.82	*d* 0.4	Ti II	12.87	V	1.175
4314.96	0.6	Ti II	14.98	V	1.156
		Fe I	15.09	III	2.188
4320.81	0.4	Sc II	20.73	III	0.603
		Ti II	20.96	V	1.160
*4325.74	0.9	Fe I	25.770	II	1.601
*4340.47	10	H_γ	40.466		10.16
4351.79	1.2	Fe II	51.77		2.693
		Mg I	51.91	IV	4.327
*4383.55	0.9	Fe I	83.548	II	1.478
4385.29	0.6	Fe II	85.39		2.766
4390.64	0.5	Mg II	90.58		9.956
*4395.01	1	Ti II	95.036	V	1.079
4399.82	*d* 0.5	Ti II	99.77	V	1.232
*4404.74	0.9	Fe I	04.752	II	1.551
4415.14	*d* 0.4	Fe I	15.13	II	1.601
4416.94	*d* 0.4	Fe II	16.81		2.766
*4443.83	1	Ti II	43.799	V	1.075

†*Separable only on two plates.*

TABLE I—*Concluded*

Stellar λ, Å	Estimated intensity	Element	Lab. wave-length	Temperature class	E.P., volts
4466.73	0.4	Fe I	66.56	II	2.819 3.005 0.110
		Fe I	66.94		3.912
*4468.50	0.9	Ti II	68.493	V	1.126
4471.50	*d* 0.4	He I	71.48		20.87
*4481.22	4	Mg II	81.327 81.129		8.825 8.826
4489.06	0.4	Fe II	89.21		2.816
4491.37	0.4	Fe II	91.41		2.843
*4501.28	0.7	Ti II	01.269	V	1.111
4505.27	0.2				
*4508.27	0.8	Fe II	08.287		2.843
*4515.35	0.8	Fe II	15.337		2.832
*4520.26	0.6	Fe II	20.238		2.795
*4522.71	0.9	Fe II	22.636		2.832
*4533.96	1	Ti II	33.966	V	1.232
4549.55	1.6	Ti II	49.62	V	1.577
		Fe II	49.48		2.816
4555.87	0.6	Fe II	55.90		2.816
4558.57	0.7	Cr II	58.66		4.056
4563.69	0.7	Ti II	63.76	V	1.216
4571.98	0.8	Ti II	71.97	V	1.565
4576.29	0.4	Fe II	76.31		2.832
4580.35	0.3				
*4583.84	0.9	Fe II	83.843		2.795
4588.21	0.6	Cr II	88.20		4.054
4618.81	0.4	Cr II	18.84		4.057
*4629.34	0.6	Fe II	29.327		2.795
4634.14	0.3	Cr II	34.12		4.055
*4861.31	10	H_β	61.327		10.16
*4924.01	0.7	Fe II	23.92		2.879
4957.59	0.3	Fe I	57.61	III	2.796
		Fe I	57.31	III	2.839
*5018.43	0.8	Fe II	18.437		2.879

References to Wave-length Table

Al. I. Fowler, A. Report on series in line spectra. Fleetway Press, Ltd., London. 1922.
Ca I. Fowler, A. Report on series in line spectra. Fleetway Press, Ltd. 1922.
Ca II. Jackson, C. B. M.N.R.A.S. 93 : 98. 1932.
Cr I. Kayser, H. and Konen, H. Handbuch der Spektroskopie. Vol. 7. S. Hirzil, Leipzig. 1924.
Cr II. Kayser, H. and Konen, H. Handbuch der Spektroskopie. Vol. 7. S. Hirzil, Leipzig. 1924.
Fe I. Burns, K. Lick Observatory Bull. 247 : 27-29. 1913.
Fe II. Russell, H. N. Astrophys. J. 64 : 194-203. 1926.
Helium. Fowler, A. Report on series in line spectra. Fleetway Press, Ltd., London. 1922
Hydrogen. Fowler, A. Report on series in line spectra. Fleetway Press, Ltd., London. 1922.
Mg I. Fowler, A. Report on series in line spectra. Fleetway Press, Ltd., London. 1922.
MgII. Fowler, A. Report on series in line spectra. Fleetway Press, Ltd., London. 1922.
Sc II. Russell, H. N. and Meggers, W. F. Sci. Paper Bur. Standards, 22 : 329-373. 1927.
Si I. Fowler, A. Proc. Roy. Soc. London, 123 : 422-439. 1929.
Si II. King, A. S. Astron. Soc. Pac. 38 : 324. 1926. Jackson, C. V. M.N.R.A.S. 94 : 723-726. 1934.
Sr II. Fowler, A. Report on series in line spectra. Fleetway Press Ltd., London. 1922.
Ti II. Crew, H. Astrophys. J. 60 : 108-121. 1924. Russell, H. N. Astrophys. J. 66 : 283-328. 1927.

strongest hydrogen lines have intensity 10; a line which is easily and distinctly visible has intensity 1.0, while a line which can be distinguished only with difficulty has an intensity of 0.3. An intensity with a "*d*" in front of it signifies a very broad and diffuse line. The values given in the table are mean values from all the plates. The identification of the line is given in the third column, while the fourth column contains the laboratory wave-length. The fifth and sixth columns give the temperature class and excitation potential respectively of the lines. These were taken from Miss Charlotte E. Moore's "Multiplet Table of Astrophysical Interest". If the term values are desired they can easily be found in Miss Moore's "Term Designations for Excitation Potentials".

All together 156 lines were found in the spectrum, and of these 147 have been identified. The following are the elements which are present:

Hydrogen. The Balmer series was measured from H_β to H_τ inclusive. These are by far the strongest lines in the spectrum, which is natural for a star of spectral class A_o. The later members of the series are all broad diffuse lines with distinct wings, so that it was impossible to measure them accurately; the measured wave-length for some lines differs considerably from the laboratory value, but they are so strong that there can be no doubt about their identification.

Helium. This is represented by the single line λ4471.48. One would expect to find λ3888, but this is undoubtedly masked by H_ζ.

Magnesium I. The diffuse triplet λ3829, 3832, and 3838 is most certainly present. λ4351 is probably also present although blended with an Fe II line. The identification of λ4167 is very doubtful as there is no sign of λ4703.

Magnesium II. This is represented by the strong doublet λ4481 which is not separable. The line λ4390 is also present.

Aluminium I. The doublet λ3944, 3961 is definitely present.

Aluminium II. Does not seem to be represented. There is a stellar line at λ3900 which coincides with a strong Al II line, but the stellar intensity is such that the observed line can be completely accounted for by the Ti II line λ3900.54.

Silicon I. Almost certainly represented by λ3905 which is the only strong Si I line in this region.

Silicon II. Represented by five lines; the doublet at λ4128, 4131 and the three lines λ3853, 3856, and 3862.

Calcium I. The strong singlet λ4227 is certainly present, but the diffuse triplets which might be expected are absent.

Calcium II. The H and K lines are the strongest lines in the spectrum with the exception of the Balmer series. The doublet at λ3706, 3737 is also present, but the intensities in the star are anomalous. The short wave component is too strong, presumably owing to a blend with an unidentified line.

Scandium I. The absence of λ3911, 4023 is conclusive evidence that Sc I is not present in the star.

Scandium II. This is represented by λ4246 and rather doubtfully by λ4321.

Titanium I. None of the strong lines of Ti I appear in the star.

Titanium II. About 31 lines can safely be attributed to Ti II. The stellar intensities are not in very good agreement with Russell's laboratory intensities, but the members of the same multiplets seem to be strengthened in the star, *i.e.*, multiplets 36 and 42.

Chromium I. A weak stellar line at λ4254 coincides with the strongest Cr I line. As this line is just visible and all other Cr I lines in this region are considerably fainter, it is not surprising that no other Cr I lines were found.

Chromium II. Represented by nine lines all of which are fairly weak.

Manganese I. There is no sign of the strong lines at λ4030 and 4033. Hence, Mn I cannot be present.

Manganese II. Definitely not represented.

Iron I. Between 50 and 60 lines are due to Fe I. All the neutral iron lines in Burn's list with an intensity greater than six are present.

Iron II. Represented by 24 lines.

Strontium I. Not present.

Strontium II. The resonance lines λ4077 and 4215 are definitely present.

The following unidentified lines were also found: 3740.1; 3743.4; 3783.3; 3858.10; 4024.61; 4177.70; 4291.77; 4505.27; 4580.35 Å.

Observed Profiles of the Balmer Lines

Determination of Line Profiles

The determination of the profile of an absorption line (*i.e.*, the distribution of intensity within the line) is the problem of translating a darkening of the photographic plate into an intensity of radiation incident on the plate. In other words, the "characteristic curve" of the photographic plate, corresponding to the wave-length in question, must be known. There are several methods of calibrating a photographic plate for such a photometric measurement, but in this investigation the calibration was obtained by the use of a neutral tint wedge. This wedge was placed in front of the slit of the spectrograph during the exposure of the plate, and in this way a variation of intensity perpendicular to the spectrum was registered at all wave-lengths. Since this variation of intensity is known from the constants of the wedge, it gives a means of relating the darkening of the plate with the intensity of incident light. This photometric method has been fully explained by Prof. H. H. Plaskett (7).

The amount of radiation absorbed must be known to determine the profile of an absorption line. In other words, the ratio of the intensity at any wave-

length in the line to the intensity that would have been present at that wave-length if no absorbing matter were present has to be found. This latter intensity is generally referred to as the background intensity. Let I_o be the incident radiation, I_λ the radiation at λ in the line, and I_c the background radiation. Then r can be determined from

$$r = \frac{I_\lambda}{I_c} = \frac{I_\lambda/I_o}{I_c/I_o}$$

A determination of r together with the corresponding distance $\Delta\lambda$ from the centre of the line enables us to plot the observed profile.

The photometric measurement of these plates was carried out by means of the recording microphotometer of the University Observatory, Oxford. A description of this instrument together with an exhaustive estimate of its performance has been given elsewhere (9). Tracings were taken of each line on each plate with this instrument, and tracings were also taken across the spectrum in the wings of each line in order to register the variation of intensity due to the wedge. On some plates two or more tracings were taken of the same line; since these were at different heights in the spectrum and, in consequence, had different intensities (and in effect, therefore, were separate exposures of the same duration), these tracings were equivalent to different plates and have been treated as such in this work.

An example of a tracing taken across H_β is shown in Fig. 1. A mean curve was drawn through the plate grain deflections, and a line through the continuous background was also drawn. In H_β it was necessary to draw the background with a slight curvature in order to obtain a smooth junction with the wings, but in some lines the background could be drawn perfectly straight across the line. Two tracings, one taken across the line and the other parallel to the line, are sufficient, when combined with a knowledge of the wedge constants, to delineate the profile. The procedure has been so clearly explained elsewhere (7, 8) that it is unnecessary to repeat it here. It is sufficient to say that the ratio I_λ/I_o for each point on the line and also the ratio I_c/I_o for the corresponding

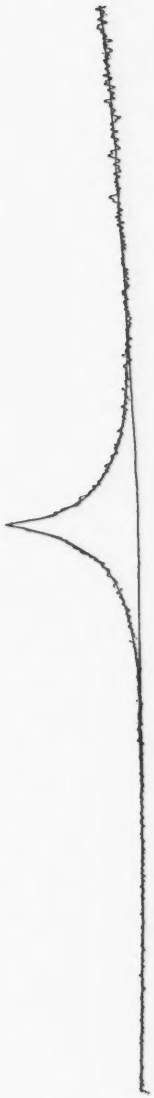

FIG. 1. *Microphotometer tracing of H_β.*

point on the background can be obtained. The ratio of these two then gives r.

The distance of each point from the centre of the line is easily obtained in terms of the grid registered on the tracing. The magnification ratio of tracing to plate travel being accurately known from the microphotometer, these measurements can be converted to millimetre distances on the plate. The problem is now reduced to translating these linear distances to Angstrom units, and this is the identical problem which was solved in the original measurement of the wave-length of the lines, so that the same procedure can be adopted, and the same constants for the Hartmann formula can be used. The curve of errors obtained from the original measurements can also be used, and when the wave-lengths are corrected in this manner they are accurate to at least 0.1 Å. It is necessary to go to this length in determining the wave-lengths in the profile because of the great width of some of the Balmer lines, which extend as far as 40 Å on either side of the centre. If linear dispersion had been assumed across the line, a marked distortion in the width of the blue and the red wings would have been introduced. When r and the corresponding wave-length for each point on the line had been determined, the profile of the line could be plotted.

Description of the Profiles

The profiles of the Balmer lines from H_β to H_ι inclusive and the K line of ionized calcium, determined by the above method, are reproduced in Figs. 2 to 9. The measurements from all the plates are shown, and the agreement

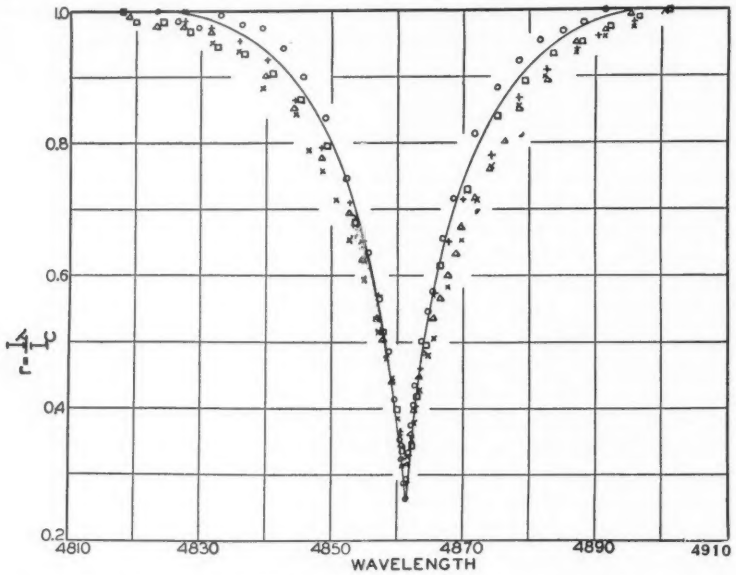

FIG. 2. *Profile of H_β.* ○, *Plate 458a;* □, *Plate 458b;* ×, *Plate 443;* △, *Plate 459;* +, *Plate 445.*

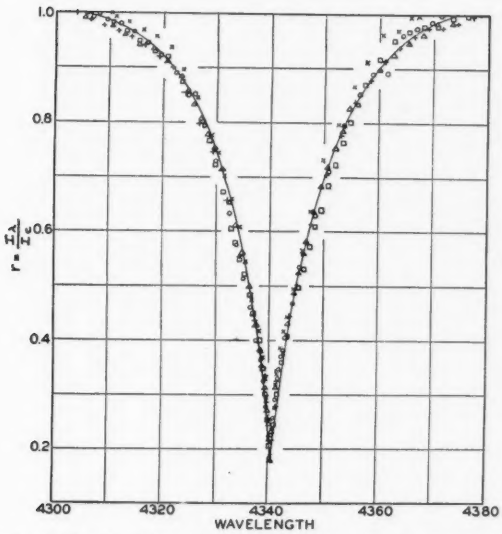

FIG. 3.—*Profile of* H_γ, ○, *Plate 458;* ×, *Plate 443;* △, *Plate 459a;* +, *Plate 445;* □, *Plate 459b.*

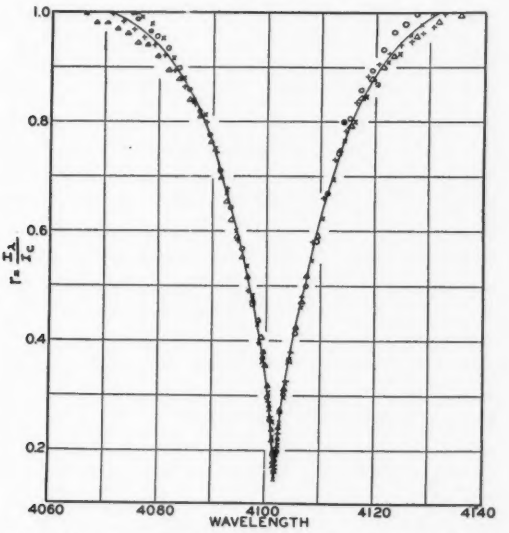

FIG. 4. *Profile of* H_δ. ○, *Plate 458;* ×, *Plate 443;* △, *Plate 459;* +, *Plate 445.*

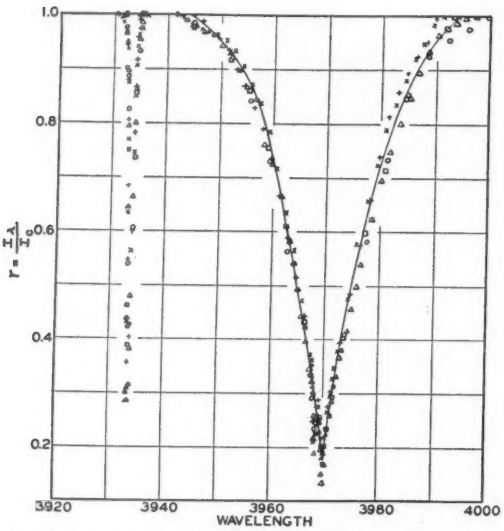

FIG. 5. *Profile of* H_ϵ. ○, *Plate 478;* ×, *Plate 443;* △, *Plate 459;* +, *Plate 445;* □, *Plate 447.*

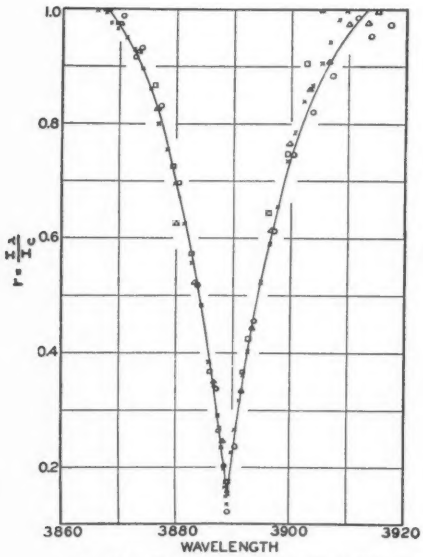

FIG. 6. *Profile of* H_ζ. ×, *Plate 443;* □, *Plate 447;* ○, *Plate 448;* △, *Plate 447a.*

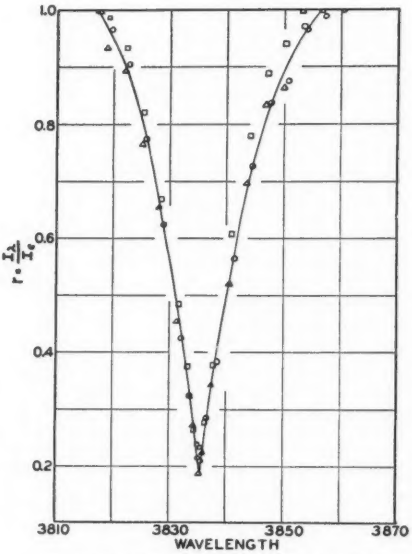

FIG. 7. *Profile of* H_η. □, *Plate 447a;* △, *Plate 447b;* ○, *Plate 448.*

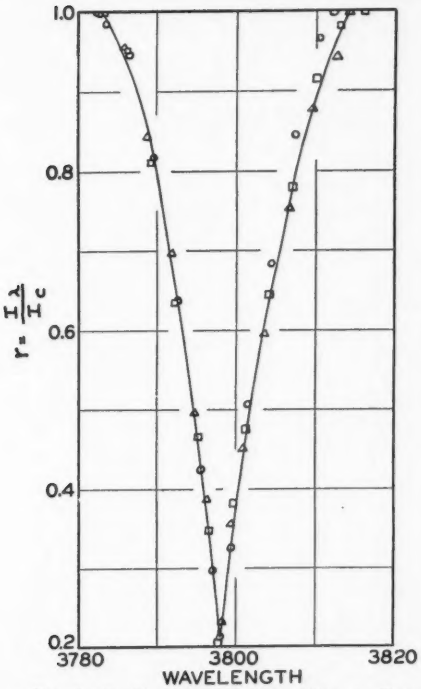

FIG. 8. *Profile of* H_θ. □, *Plate 447a;* △, *Plate 447b;* ○, *Plate 448.*

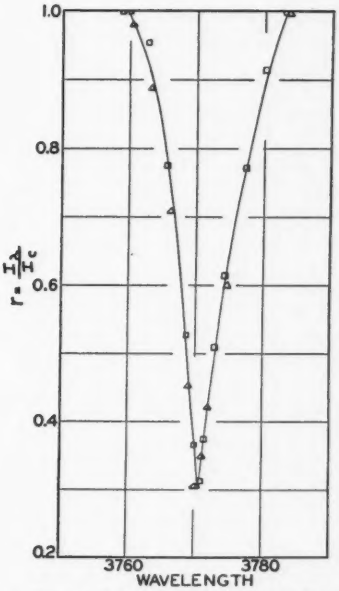

FIG. 9. *Profile of* H_ι. □, *Plate 447a;* △, *Plate 447b.*

between the different sets of measurements is very striking. There is very little scatter in the readings except in the extreme wings of the lines where an exact agreement is hardly to be expected, since in this region a very small error in the position of the background would be very pronounced. The most unsatisfactory of all the profiles is that due to H_β, where a large difference in the profiles determined from the different plates even in the core of the line is found. It was obvious that there must be some reason for the fact that this line was so much less satisfactory than the others, and an examination of the focus test plates immediately showed where the trouble lay. Of the four plates only one, 458, was in focus at H_β, although all were quite satisfactory for the rest of the spectrum. A second tracing taken from this plate was then measured and good agreement with the first tracing was found except for some small scatter in the wing. A mean profile given by the two tracings from 458 has been used for all measurements, although the readings from all the plates are reproduced in the figure.

That this lack of focus on the plates should show up in the profile for H_β is a strong recommendation for the resolving power of the photometric method. The agreement of the profiles of the other lines is a further proof of this.

In each of the figures a mean profile has been drawn, and in Table II the values for r and the corresponding $\Delta\lambda$ are given for points on the profiles. The H line of ionized calcium appears in the violet wing of H_ϵ, but since this line is very narrow and not accurately delineated it has not been included in the mean profile.

TABLE II

MEAN LINE PROFILES

Line	$r = \frac{I_\lambda}{I_c}$	$\Delta\lambda$ (violet wing), Å	$\Delta\lambda$ (red wing), Å	Line	$r = \frac{I_\lambda}{I_c}$	$\Delta\lambda$ (violet wing), Å	$\Delta\lambda$ (red wing), Å
H_β	1.00	33.2	35.0	H_γ	1.00	35.0	33.6
	.98	28.0	28.1		.98	29.9	28.5
	.95	22.5	22.8		.95	24.4	23.9
	.90	17.1	17.3		.90	18.5	19.2
	.85	13.9	13.7		.85	15.4	15.8
	.80	11.4	11.1		.80	13.1	13.6
	.70	8.1	7.5		.70	9.3	10.0
	.60	5.0	4.8		.60	6.6	7.3
	.50	2.9	2.7		.50	4.4	4.6
	.40	1.2	1.3		.40	2.3	2.6
	.30	0.2	0.5		.30	0.8	1.1
	.262	0.0	0.0		.20	0.2	0.2
					.18	0.0	0.0
H_δ	1.00	30.9	30.5	H_ϵ	1.00	26.5	23.7
	.98	26.9	27.6		.98	23.9	21.6
	.95	23.0	24.1		.95	20.0	19.1
	.90	18.9	29.3		.90	16.1	16.0
	.85	16.0	16.2		.85	13.9	14.0
	.80	13.7	13.9		.80	12.1	12.2
	.70	10.1	10.3		.75	10.8	10.9
	.60	7.6	7.7		.70	9.5	9.5
	.50	5.1	5.3		.60	7.1	7.0
	.40	3.0	3.1		.50	5.1	4.9
	.30	1.6	1.4		.40	3.2	3.0
	.20	0.2	0.2		.30	1.5	1.7
	.16	0.0	0.0		.20	0.2	0.2
					.17	0.0	0.0
H_ζ	1.00	21.1	23.8	H_η	1.00	18.2	20.5
	.98	19.6	21.4		.98	17.0	19.3
	.95	17.7	20.0		.95	15.5	17.2
	.90	15.0	17.1		.90	13.3	14.6
	.85	13.0	15.0		.85	11.6	12.5
	.80	11.6	13.0		.80	10.4	10.7
	.70	9.1	10.0		.70	8.1	8.2
	.60	7.1	7.4		.60	6.3	6.2
	.50	5.2	5.4		.50	4.5	4.5
	.40	3.6	3.7		.40	2.9	2.9
	.30	1.9	2.0		.30	1.5	1.3
	.20	0.7	0.6		.20	0.1	0.1
	.13	0.0	0.0		.188	0.0	0.0
H_θ	1.00	14.9	16.1	H_ι	1.00	11.0	12.3
	.95	12.0	13.9		.95	8.7	10.7
	.90	10.2	12.1		.90	7.0	9.3
	.85	9.0	10.9		.85	5.9	8.2
	.80	8.1	9.5		.80	5.2	7.0
	.70	6.5	7.2		.70	4.2	5.2
	.60	5.0	5.2		.60	3.0	3.3
	.50	3.2	3.6		.50	2.2	2.1
	.40	1.9	2.2		.40	1.1	1.0
	.30	0.9	1.0		.30	0.1	0.1
	.207	0.0	0.0		.282	0.0	0.0

TABLE II—*Concluded*

MEAN LINE PROFILES—*Concluded*

Line	$r = \frac{I_\lambda}{I_c}$	Δλ (violet wing), Å	Δλ (red wing), Å	Line	$r = \frac{I_\lambda}{I_c}$	Δλ (violet wing), Å	Δλ (red wing), Å
Ca II K-line							
	1.00	2.0	1.8		.70	0.4	0.5
	.98	1.4	1.4		.60	0.3	0.4
	.95	1.1	1.1		.50	0.2	0.3
	.90	0.7	0.8		.40	0.1	0.2
	.85	0.6	0.6		.30	0.05	0.05
	.80	0.6	0.6		.284	0.00	0.00

In much of the literature the intensity of a spectral line is expressed as a half-width, *i.e.*, the total width over which the absorption is greater than half the maximum. This value as determined above for the Balmer lines of α-Lyrae is given in Table III. The central intensity of the lines has also been included.

TABLE III

Line	Half-width, Å	Central intensity, $r = \frac{I_\lambda}{I_c}$
H_β	11.6	0.26
H_γ	13.3	0.18
H_δ	14.1	0.16
H_ϵ	13.5	0.17
H_ζ	12.9	0.12
H_η	12.1	0.19
H_θ	10.3	0.21
H_ι	7.7	0.28

The half-width increases with the series up to H_δ, where a maximum occurs, and then it steadily decreases towards the series limit. A minimum value for the central intensity occurs at H_ζ. The fact remains, however, that there is great similarity, both with regard to shape and size, in the four lines H_γ, H_δ, H_ϵ, and H_ζ. The only pronounced difference is that the wings are slightly less extensive in the later members of the series. Beyond H_ζ the lines rapidly become narrower and less intense. This may be due to the overlapping of the wings of the lines, but an examination of the tracings did not seem to indicate such an overlapping for lines of wave-length shorter than H_θ. However, since other investigators have found this overlapping even as early as H_δ (4, p. 282), too much emphasis cannot be placed on the fact that the author's lines appear to become both shallower and narrower, as we proceed beyond H_ζ, as this might quite well be due to the overlapping. For lines of wave-length shorter than H_ζ, however, the author places full reliance on the profiles. There does not appear to be any indication of asymmetry in any of the lines.

Total Absorptions

To obtain the total absorption (or equivalent width), $\int_{-\infty}^{+\infty}(1-r)d\lambda$, of a line is a comparatively simple matter once the profile has been determined. It is most easily done by plotting $1-r$ against λ and integrating the area under the curve with a planimeter. The total absorption, which has the dimensions

of a length, is usually expressed as Angstroms of continuous spectrum, and this method has been followed here. For profiles of the hydrogen lines and that of the calcium K-line, the mean value of r, as obtained from the curves, was used to plot $1-r$, and the area under this mean curve was taken as the equivalent width. In the weaker metallic lines, however, the irregularities due to the plate grains were comparable in size to the absorption line itself; this made it extremely difficult to draw a mean profile. In this case it seemed preferable to plot $1-r$ for each individual tracing, determine the corresponding equivalent width, and take the mean of these values for the total absorption. By taking a sufficient number of tracings the spurious effects due to the silver grains should be eliminated. This method differs from that used by Struve and Elvey (11, p. 416). They measured the base and central intensity of the line on the tracing and then computed the area by assuming the line to have a triangular contour.

In Table IV are given, not only those results obtained in this investigation, but also, for comparison purposes, the total absorptions from all previous investigations of the spectrum of α-Lyrae.

A study of this table shows that the results obtained in this investigation are not always in agreement with previous observations. The absorptions obtained by Elvey for H_β and H_γ are considerably larger than those obtained by the author. The other observers, however, give better agreement, and when the present determinations are compared with the mean of all the others as given in the last column, the agreement is fully as good as one might expect. The experimental conditions of the present investigation were such that the author feels justified in placing considerable reliance on the results even when they are at variance with other observations. The following considerations lead us to this conclusion:

(1) The large resolving power of the plates, coupled with the excellent performance of the microphotometer.

(2) The dispersion of the plates (23 Å per mm. at H_β; 10.92 Å per mm. at H_δ). It has been suggested by Minnaert (6, p. 329) that a large dispersion gives a greater total absorption than a small dispersion, and it seemed as if this might account for the fact that the total absorptions obtained by the author are larger than those of Elvey. There was, however, an opportunity to test this, as both one-prism and two-prism plates were available in the region λ3900 to λ4000. The hydrogen lines H_ϵ and H_ζ and the K-line of Ca II are in this region, and the fact that no difference in the profiles of these lines as determined from the one-prism and the two-prism plates was found seems to contradict Minnaert's observation, at least within the limits of the dispersion.

(3) Because of the nature of the plates it was possible to measure spectra with large variation in the blackening of the plate, but with identical exposure times. Hence, in effect, an infinite series of spectra of varying intensity are available, so that it is possible to measure the line profile at any intensity.

TABLE IV

No. of tracings	Line	Present investigation		Struve & Elvey (11, p. 418) (log A)	Elvey (2)	Gunther (5)	Williams (15)	Dunham (1)	Williams (16)	Elvey & Keenan (3, p. 224)	Mean of all measurements except the present
		$A = \int_{-\infty}^{+\infty}(1-r)d\lambda$	log A								
2	H_β	12.01	1.08		18.18	14.7	12.9			18.2	16.0
5	H_γ	14.37	1.16		21.18	15.1	15.58	13.9	18.1	21.2	17.5
4	H_δ	14.98	1.18			16.6	12.92	13.4	16.19	14.9*	14.8
5	H_ϵ	13.30	1.12			14.2		13.89			14.1
4	H_ζ	13.45	1.13			13.5					13.5
3	H_η	11.33	1.05			13.4					13.4
3	H_θ	9.15	0.96			9.8					9.8
2	H_ι	6.12	0.79			6.5					6.5
5	Ca II (3933)	0.648	−0.19						0.93		0.93
9	Ca I (4227)	0.057	−1.24	−1.12							0.076
15	Mg II (4481)	0.293	−0.53	−0.29							0.513
4	Sr II (4215)	0.036	−1.44	−1.35							0.045
4	Sr II (4078)	0.046	−1.34								
4	Si II (4128)	0.062	−1.21								
4	Si II (4130)	0.060	−1.22								
4	Fe I (4063)	0.058	−1.24								
4	Fe I (4072)	0.041	−1.39								
4	Fe II (4179)	0.064	−1.19								
4	Fe II (4233)	0.061	−1.21	−0.91							

Single prism.

The fact that the profiles, as measured on the different plates and at different wedge heights, all agreed is fairly conclusive evidence of the reliability of the measurements. It seemed worth while also to make a detailed comparison of the total absorptions to determine if there was any variation with intensity. The results for the lines λ4481 Å of Mg and λ4227 Å of Ca are given in Tables

V and VI. The column headed "transmission in the continuous spectrum" gives the ratio of the light transmitted through the continuous spectrum at the wedge height in question to that transmitted through the unexposed plate, and thus gives an indication of the blackening of the plate.

TABLE V

λ4481Å

Plate 443		Plate 459		Plate 458		Plate 445	
Transmission in cont. spec.	A	Transmission in cont. spec.	A	Transmission in cont. spec.	A	Transmission in cont. spec.	A
0.420	0.272	0.282	0.258	0.360	0.339	0.324	0.346
0.345	0.250	0.254	0.328	0.268	0.278	0.310	0.359
0.292	0.232	0.140	0.292	0.126	0.284	0.106	0.270
0.234	0.248						
0.222	0.254						
0.189	0.266						
Mean	0.254		0.293		0.300		0.325

Mean of four plates: 0.293.

TABLE VI

λ4227 Å

Plate	Transmission in cont. spec.	A
443	0.444	0.049
459	0.342	0.050
443	0.318	0.066
458	0.246	0.069
443	0.233	0.068
443	0.225	0.066
443	0.186	0.035
445	0.185	0.066
443	0.160	0.045

There is no indication of any systematic change of total intensity with the blackening, and these measurements, combined with the fact that good agreement was found in the hydrogen profiles as determined at different heights, leads the author to assert that within certain limits the total absorption is independent of the blackening on the plate. With the line λ4481 Å, however, it is found that the readings from Plate 443 are considerably smaller than those from the other plates. This is difficult to account for. The plates were all equally well focused at this wave-length. None of the other lines seem to show this effect; this argues against instrumental errors. The fault could hardly lie in the calibration curve, as the readings from Plate 443 are consistent among themselves. It almost seems as if there must have been some intrinsic change in the absorption line at the time when Plate 443 was exposed, although it is difficult to account for such a variation in the intensity of a line. For the purpose of tabulation the mean of the four plates was taken, each plate being given equal weight.

(4) It is probable that a large part of the discrepancy between the results obtained by the different observers arises through the uncertainty in the position of the continuous background (4, 17). Elvey and Struve have shown that when they compute the total absorption of a line, using continuous

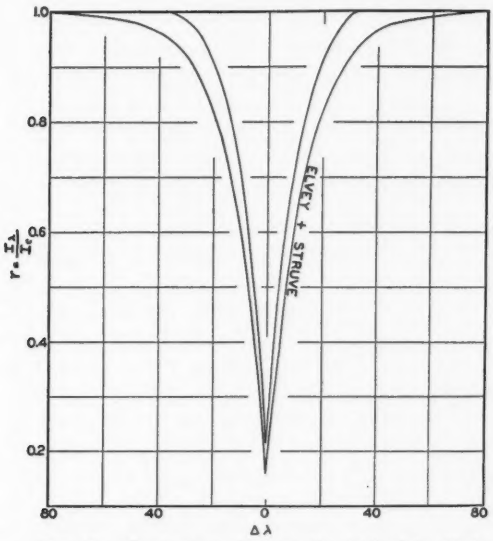

FIG. 10. *Comparison of the profile obtained for H_γ by Elvey and Struve with that obtained in this investigation.*

backgrounds that differ by 1 mm. on their tracing, the results that they obtain differ by 18%. If the position of the background as it is drawn on their tracings is compared with the present tracings, it appears as if the background has been drawn consistently lower than theirs. In Fig. 10 is shown a comparison between the profile of H_γ given by them (4, p. 283) with that obtained from Plate 458. It is immediately evident that their line is much wider. In order to see if this difference could be due to the position of the background, a determination was made of the position in which the background would have had to be drawn in order to make the present profile coincide with theirs. This background is shown as a broken line in Fig. 11. It is quite clear that it would be impossible to draw the background in this position. The position of the background, therefore, cannot account for all the difference between Elvey and Struve's profiles and those obtained in this investigation. A wider line and a larger total absorption could have been obtained by draw-

FIG. 11. *Microphotometer tracing of H_γ. The broken line shows how background must be drawn to make profile coincide with that of Elvey and Struve.*

ing the background higher, but there does not seem to be any justification for this. A study of tracings taken with smaller magnification shows that there is no reason for believing that the continuous background does not go straight across the line, and that once outside of the wings of the line the tracing does not register the background. Hence, the mean position of the plate grain deflections should give the continuous spectrum, and on this basis the background has been drawn.

Conclusion

The profiles of the Balmer lines which have been presented in this paper are available as a means of testing any theoretical formulas which may be advanced as an explanation of the formation of absorption lines in A_o stars. All the formulas which are at present available were tested during this investigation without any satisfactory results. Neither a natural radiation damping formula similar to that employed by Unsöld (12, 13, 14), nor the use of a Doppler absorption coefficient will produce a theoretical formula that agrees with the observed Balmer profiles. The most hopeful line of attack seems to be that given by Pannekoek and Verwey (10) in which they apply the Stark effect to the broadening of the hydrogen lines in early type stars. The theoretical lines which they obtained are very similar in shape to the author's observed Balmer lines, and a satisfactory explanation may be obtained in this way.

The total absorptions should lend themselves very easily to a determination of the relative abundance of the different elements in the star. A knowledge of the curve of growth connecting the observed total absorptions with the number of atoms is required. With this curve it would be possible to estimate directly the ratio of hydrogen to the metallic atoms in the star, a problem of great importance to Astrophysics. Other results will also follow, such as an estimate of the electron pressure and the temperature at the point at which the lines originate in the stellar atmosphere.

Acknowledgment

The author wishes to express his thanks to Prof. H. H. Plaskett of the University Observatory, Oxford, who made this investigation possible. He not only suggested the problem and furnished the plates, but throughout the investigation made many helpful suggestions and gave every possible assistance.

References

1. Dunham, T. Jr. Harvard Circular, 853.
2. Elvey, C. T. Astrophys. J. 71 : 191-208. 1930.
3. Elvey, C. T. and Keenan, P. C. Astrophys. J. 74 : 223-224. 1931.
4. Elvey, C. T. and Struve, O. Astrophys. J. 72 : 277-300. 1930.
5. Gunther. Z. Astrophys. 7 : 118. 1933.
6. Minnaert, M. Observatory, 57 : 328-342. 1934.
7. Plaskett, H. H. Pub. Dom. Aph. Ob. 2 : 213-259. 1923.
8. Plaskett, H. H. M.N.R.A.S. 91 : 870-933. 1931.
9. Plaskett, H. H. M.N.R.A.S. 95 : 160-179. 1934.
10. Pannekoek, A. and Verwey, S. K. Akad. Amsterdam Proc. 38 : 479-489. 1935.
11. Struve, O. and Elvey, C. T. Astrophys. J. 79 : 410-440. 1934.
12. Unsöld, A. Z. Physik, 44 : 793-809. 1927.
13. Unsöld, A. Z. Physik, 46 : 765-781. 1928.
14. Unsöld, A. Z. Physik, 59 : 353-377. 1930.
15. Williams, E. G. Solar Phys. Observatory, Cam. 2 : 2. 1932.
16. Williams, E. T. R. Harvard Circular, 348.
17. Williams, E. T. R. Astrophys. J. 72 : 127-130. 1930.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 15, SEC. B. OCTOBER, 1937 NUMBER 10

THE OXIDATION OF METHANE AT HIGH PRESSURES

II. EXPERIMENTS WITH VARIOUS MIXTURES OF VIKING NATURAL GAS AND AIR[1]

BY E. H. BOOMER[2] AND VICTOR THOMAS[3]

Abstract

Mixtures of a natural gas, substantially methane, and air in various proportions were passed over catalysts, and the effects of the variables, composition of mixture, pressure, temperature, and space velocity, were determined. Similar experiments were made with mixtures of methane and air. Mixtures containing from less than 3% to more than 13% of oxygen as air were used. The temperature range was 350° to 500° C. and the pressure range 140 to 230 atm. Methanol was the principal product, and yields as high as 74% on the basis of carbon oxidized were obtained. Copper was the principal catalyst used. Traces of sulphur poisoned the catalyst very effectively.

Introduction

In a previous report (2) some preliminary investigations on the direct oxidation of natural gas of high methane content under pressure were described. The present report gives results obtained in a systematic investigation of the subject in which natural gas from the Viking field and air as the source of oxygen were used. Massive copper, shown previously (2) to be an effective promoter of the reactions, was used exclusively in the experiments as a catalyst. The effects of composition of the gas mixture, the temperature of the reaction, the pressure, and the rate of flow of gas through the reactor were determined.

Equipment was designed and built which permitted more exact control of the variables affecting the reaction than was possible with the original equipment. The method used in this work resolved itself into bringing separately the gas and air in the desired proportions to a mixer immediately preceding the reactor, passing the mixed gas through the reactor to a high pressure condenser, and then through an expansion valve. After expansion, the off-gases were stripped of condensable materials, samples were taken for analysis, and their volumes measured.

[1] *Manuscript received May 31, 1937.*
Contribution from the Chemical Laboratories, University of Alberta, Edmonton, Canada, with financial assistance from the Carnegie Corporation Research Grant to the University of Alberta, and equipment provided by the National Research Council of Canada and the Research Council of Alberta.

[2] *Associate Professor of Chemistry, University of Alberta.*
[3] *Demonstrator, Department of Chemistry, University of Alberta, 1934-1935.*

Experimental

Materials

Natural gas from the Viking field, east of Edmonton, Alberta, was used throughout. Its composition was reasonably constant at 90.8% methane, 3.5% ethane, and 5% nitrogen by volume, as obtained by means of the improved Bureau of Mines type of Orsat apparatus. Actually, the gas contained propane in small amounts and the analysis is merely conventional. Such analyses, in the present work, serve to reveal the total carbon content of the gas, which is the element of interest. The gas also contained small amounts of the vapors of organic sulphur compounds added as an odorant. The sulphur was removed completely in the apparatus to be described.

Air was used as a source of oxygen and was dried by passage over calcium chloride before compression. Carbon dioxide was removed from the compressed air, and a further drying carried out by passage over solid potassium hydroxide.

Pieces of electrolytic copper, $\frac{3}{16}$ in. square and $\frac{3}{32}$ in. thick, were used as catalyst. The weight of copper used was 39.8 gm. and its actual volume was 4.46 cc. The effective volume of the catalyst including free spaces was approximately 12 cc. The copper was activated by alternate oxidation and reduction prior to use. Air was used as an oxidizing agent and a mixture of hydrogen and methanol vapor as a reducing agent. This catalyst was very sensitive to poisoning by sulphur and the vapors of heavy hydrocarbons. The activity of the catalyst was restored either by activation as described above, or by immersion in dilute nitric acid for a short time. Copper in the form described was used in virtue of the good heat conductivity obtained. With exothermic reactions such as were investigated, the control of temperature becomes difficult if not impossible unless provision is made for rapid dissipation of heat.

Apparatus and Procedure

The compressed air and natural gas were stored in cylinders of such capacity that the pressure drop during an experiment would be relatively small, approximately 2 to 3 atm. The gas was stored at the pressure desired in the experiment, and the air was stored at a pressure some 35 atm. higher. The gas passed through concentrated sulphuric acid, solid potassium hydroxide, and activated charcoal to the reactor system, as described previously (2); thus sulphur was eliminated. The air was passed through solid potassium hydroxide before it entered the reactor system. Both lines included a check valve in front of the control valves on the reactor system to prevent accidental entry of air into the natural gas system.

The apparatus used to study the oxidation reactions is shown conventionally in Fig. 1. The gas and air were admitted through valves 1 and 2, both of which were so designed as to be capable of very fine adjustment. They were also equipped with electric heaters. The valve connected to the air supply was heated in order to counteract the cooling effect of a 35 atm. pressure drop and so maintain a constant rate of flow. The gas and air met in the mixer *A*.

The central hole of the mixer contained a snugly fitting piston, *B*, which had a shallow spiral groove cut along its length. The bottom of the piston fitted a ground seat in the mixer and acted as a check valve against explosions in the reactor; thus additional protection against mixing of the contents of the storage cylinders was obtained. From the mixer, *A*, a sample of the gas

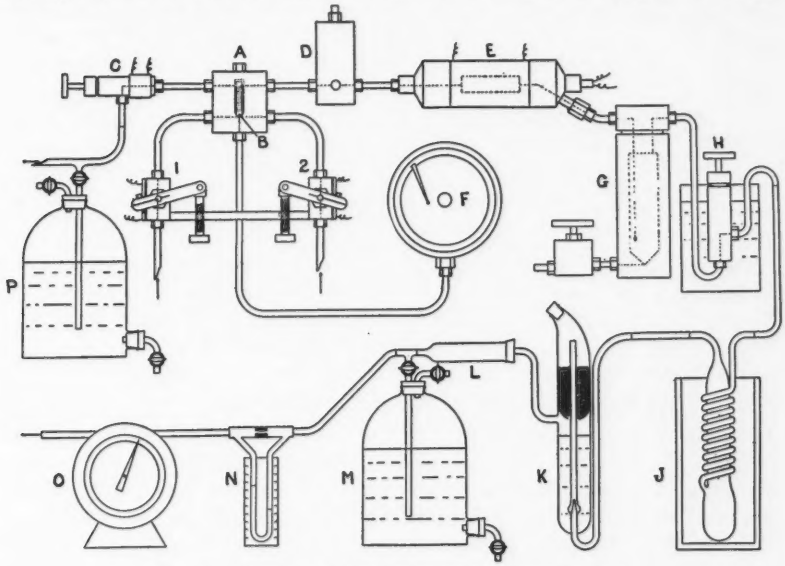

FIG. 1. *Diagram of high pressure oxidation apparatus.*

mixture was removed continuously through the heated expansion valve, *C*. A record of the pressure during an experiment was obtained by means of a Bourdon Tube type recording gauge, *F*. This gauge was calibrated at intervals by means of a dead-weight piston gauge. From the mixer, the gas passed through a short tube to the reactor, *E*. A spring controlled relief valve, *D*, in the line was set to open at 50 atm. above the operating pressure.

The reactor, *E*, is shown in detail in Fig. 2. The body, *B*, was constructed of high nickel-chromium steel, and was heated electrically as shown. All other parts were cut from chrome-molybdenum steel bar. The inlet tube, *A*,

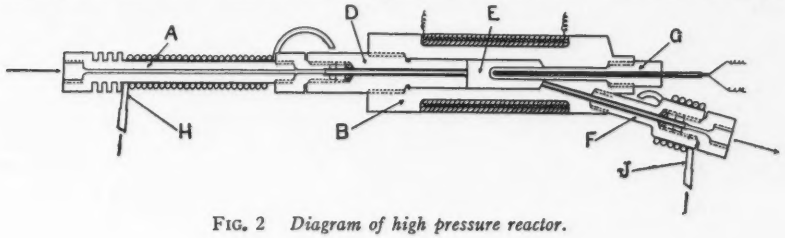

FIG. 2 *Diagram of high pressure reactor.*

and closure, *D*, were cooled by running water in the tube *H*; the outlet tube, *F*, was similarly cooled by water in the tube *J*. Both the closure, *D*, and outlet tube, *F*, were fitted with a lining of $\frac{1}{8}$ in. copper tubing, and all the interior surfaces of the reactor were copper plated. The temperature in the interior of the reactor was obtained by means of a thermocouple fitting the well, *G*. The temperature was measured on a recording potentiometer which controlled the power input to the heater, and maintained the temperature constant to within 2° C. The catalyst was placed in the space, *E*, of volume 12.7 cc.

From the reactor, the products of reaction passed through copper tubing to the chromium plated, high pressure, condenser, *G*, Fig. 1, the uncondensed gases passing on to the heated expansion valve, *H*. From the point of entry of the gases to the reactor closure, the gases and products were not allowed to come in contact with ferrous metals.

After expansion, the gaseous products passed through the ice-cooled condenser, *J*, the water scrubber, *K*, the calcium chloride tube, *L*, the flow meter, *N*, and the wet-test meter, *O*. A continuous, proportional sample of the off-gases was taken throughout an experiment by means of the sampler shown in part as *M*.

The composition of the inlet gas mixture was controlled by continuous analysis, in a thermal conductivity cell, of the sample expanded through valve, *C*. At the same time, a continuous proportional sample was collected in bottle *P*. The thermal conductivity analysis apparatus was of the usual type. Two cells of about 3.5 cc. volume were cut in a copper block and fitted with identical coils of 0.0015 in. platinum wire, heated by a constant current. The wires formed two arms of a Wheatstone bridge. Pure dry air was passed at a constant rate of 10 cc. per min. through one cell, and the air-gas mixture was passed through the other cell at the same rate. The setting of the Wheatstone bridge to give balance was used as a measure of the composition. The instrument was calibrated by using known gas-air mixtures, and it readily showed a variation in composition of 0.2%. Previous to an experiment, the bridge was set for the desired composition. The gas valve, 1, was opened and then the air valve, 2, Fig. 1, was opened carefully and adjusted until the bridge galvanometer showed no deflection. Adjustment was continued throughout an experiment according to the movements of the galvanometer index. The lag between the time of mixing at *B* and the time the expanded gas mixture entered the analyses apparatus was about one minute. This method of nearly instantaneous, continuous analysis and control of the air-gas mixture was highly satisfactory.

The rate of flow of gas through the reactor was controlled by adjustment of the expansion valve, *H*. This valve, of non-ferrous materials, was constructed and fitted so as to be capable of fine adjustment and of staying in adjustment. It was necessary to keep the bath temperature fairly constant at 90° C. or higher to prevent erratic variations in rate of flow.

The procedure, after an experiment, has been described (2). Both the average in-gas and off-gas samples in bottles P and M were analyzed by conventional methods. The liquid products were collected and aliquot parts taken for determination of methanol, formaldehyde, formic acid, and occasionally, other constituents. As a check on the accuracy of the analytical methods, ultimate analyses were carried out occasionally for carbon and hydrogen. The standard method of carbon and hydrogen determination by combustion was used for the liquid condensate. Precise ultimate analysis of the gas was carried out by a method already described (3), the principles of ultimate organic analysis being used. The calculated amounts of carbon and hydrogen based upon the analysis for individual constituents were more than 98% of the values found by ultimate analysis. This left no doubt as to the accuracy of the analytical methods, and showed that the quantity of carbon compounds other than those tested for was negligible.

Results and Discussion

The results are given in the form of tables of data, and general features are illustrated by graphs. No experimental means was available for determining the actual volume of the in-gas, and an indirect method was used. The method consisted of the calculation of the weight of all the carbon in the products of the reaction, and, with the analysis of the in-gas, the volume ratio of in-gas to off-gas could be found. The method assumes, of course, that all the carbon entering the system was accounted for in the products. Every precaution was taken to ensure that this was true. In all the experiments tabled, except one noted, no carbon or compounds of carbon were deposited in the high pressure system. The analyses were all carried out in duplicate and checks obtained. Further, as described previously, the analytical methods were confirmed by ultimate analysis for carbon and hydrogen. Nevertheless some doubt arises as to the correctness of the results. On the basis of a carbon balance, the other three elements involved, nitrogen, hydrogen, and oxygen, did not show a good balance except rarely. The discrepancy in the nitrogen and hydrogen balances was commonly small, but it frequently exceeded experimental error. Generally, duplicate experiments agreed with each other, and no explanation can be offered for the discrepancies. The oxygen balances showed very great errors, sometimes positive but mostly negative. The errors were far beyond any experimental error conceivable. Many attempts to trace the oxygen discrepancy were made without any success. Among other tests, measurements of the volume of in-gas were made directly by pressure drop in the storage cylinder. While not very accurate, the agreement with the calculated volume was within the limits of error. The oxygen discrepancy was traced almost certainly to the reactor and catalyst, but no explanation was found. The phenomenon is not new and was reported by Wiezevitch and Frolich (5), also with no explanation.

Ignition Temperature and Explosions

Some preliminary experiments with high oxygen concentration made to determine the ignition temperature are given in Table I. Temperatures of 250° and 300° C. did not produce any reaction, but at 350° C., as in experiment

TABLE I

PRELIMINARY EXPERIMENTS AT 350° C. AND HIGH OXYGEN CONCENTRATIONS

Experiment No.	49	50	51	52
Pressure in atm.	147	150	150	199
Off-gas flow, litres per min.	0.80	0.51	0.84	0.84
In-gas analysis				
O_2	14.9	14.9	15.0	14.8
CH_4	26.2	26.2	26.7	26.6
C_2H_6	0.87	0.87	0.85	0.88
N_2	58.03	58.03	57.45	57.72
Off-gas analysis				
CO_2	1.4	3.0	2.81	3.9
O_2	1.46	2.2	0.75	0.80
H_2	2.1	1.1	1.44	2.60
CO	3.0	3.8	4.02	4.40
CH_4	23.1	24.4	23.9	23.6
C_2H_6	2.2	0.4	0.49	0.80
N_2	66.8	65.1	66.6	63.9
Volume in-gas / Volume off-gas	1.22	1.15	1.13	1.19
Condensate, gm. per 100 l. in-gas at N.T.P.				
CH_3OH	0.018	0.264	0.246	0.291
CH_2O	0.013	0.086	0.088	0.051
HCOOH	0·0	0·0	0·0	0·0
H_2O	9.04	8.99	9.10	11.42
Alcohol in condensate, %	0.198	2.84	2.60	2.48
Total carbon oxidized, %	13.0	22.1	22.1	25.6
Yields, as % of total carbon burned to:				
CH_3OH	0.348	3.01	2.76	2.84
CH_2O	0.275	1.04	1.05	0.53
HCOOH	0·0	0·0	0·0	0·0
Total	0.623	4.05	3.81	3.35
Total inlet oxygen accounted for, %	62.3	79.8	71.6	88.4

No. 49, vigorous reaction occurred and explosions took place. During the explosions, a copious deposit of soft carbon was formed on the catalyst; this deposit was caused probably by pyrolysis of methane and by the decomposition of oxidation products. While a material balance is given for No. 49, it is incorrect in not including the deposited carbon. The explosions were promoted by steel surfaces, and when reaction was confined to copper surfaces, they did not occur. Experiments 50, 51, and 52 are such experiments, and in no case was any carbon deposited in the apparatus. The yields are small and independent for all practical purposes of pressure and rate of flow.

Some information on the effect of pressure was given by these preliminary experiments. The effect of a 50 atm. increase was so small as to be almost negligible. Yields were lowered, and the amount of carbon burned increased slightly.

Effect of Oxygen Concentration

The effect upon the reactions of inlet oxygen concentration is illustrated by the data given in Table II and by Graphs I and II, Fig. 3. The yield of

TABLE II

EXPERIMENTS AT 350° C. AND 185 ATM. PRESSURE, SHOWING THE EFFECT OF OXYGEN CONCENTRATION ON YIELD

Experiment No.	76	77	66	67	60	69	58	59
Off-gas flow, litres per min.	0.85	0.78	0.84	0.86	0.83	0.83	0.80	0.82
In-gas analysis								
O_2	3.47	3.76	6.15	8.45	10.8	10.33	12.0	13.2
CH_4	78.0	76.4	63.8	54.0	43.8	46.8	38.8	33.4
C_2H_6	1.02	1.88	2.11	1.79	1.45	1.21	1.21	1.1
N_2	17.51	17.96	27.94	35.76	43.95	41.66	47.99	52.3
Off-gas analysis								
CO_2	0.53	0.61	1.26	1.76	3.29	2.15	3.31	3.52
O_2	0.21	0.32	0.21	0.74	0.55	0.68	0.65	0.52
H_2	0.53	0.47	0.56	0.82	0.53	1.16	1.17	1.03
CO	1.30	1.21	1.98	2.57	1.22	3.23	2.11	1.97
CH_4	78.7	77.8	68.1	55.8	47.1	45.1	40.1	34.2
C_2H_6	0.65	1.1	0.38	0.31	0.51	0.12	0.1	0.63
N_2	18.08	18.49	27.5	38.0	46.8	47.56	52.6	58.13
Volume in-gas / Volume off-gas	1.04	1.04	1.1	1.08	1.15	1.07	1.14	1.17
Condensate, gm. per 100 l. in-gas at N.T.P.								
CH_3OH	1.74	1.73	2.16	2.06	1.46	1.84	1.37	0.96
CH_2O	0.195	0.198	0.202	0.159	0.137	0.126	0.114	0.101
HCOOH	0.034	0.031	0.049	0.063	0.015	0.061	0.016	0.011
H_2O	2.76	2.46	5.07	6.32	7.67	8.98	8.64	8.73
Alcohol in condensate, %	36.9	39.0	28.8	23.9	15.7	16.7	13.5	9.82
Total carbon oxidized, %	3.94	3.92	6.73	9.73	10.8	13.1	14.2	15.3
Yields, as % of total carbon burned to:								
CH_3OH	38.7	38.8	33.2	25.9	20.3	20.0	16.5	12.34
CH_2O	4.64	4.75	3.32	2.12	2.02	1.45	1.46	1.39
HCOOH	0.52	0.48	0.52	0.51	0.14	0.46	0.14	0.10
Total	43.86	44.03	37.04	28.54	22.46	21.91	18.1	13.73
Total inlet oxygen accounted for, %	107.0	99.0	101.4	95.0	85.0	101.2	86.3	81.5

useful products falls off linearly with an increase in oxygen concentration in the mixture. The slope of Graph I, giving total yield, is about -3.1, which may be considered a large rate of increase of yield with decreasing oxygen concentration. Graphs I and II show convergence at the higher

oxygen concentration; this shows that the proportion of formaldehyde and formic acid is nearly constant, lying between 10 and 11% of the total yield. The production of water and carbon oxides increases regularly with increasing oxygen concentration. As would be expected, the concentration of methanol in the condensate parallels the yield, and the relation to oxygen concentration is linear. Evidently, low oxygen concentrations are necessary for high yields of useful products, and also, for high concentrations in the condensate.

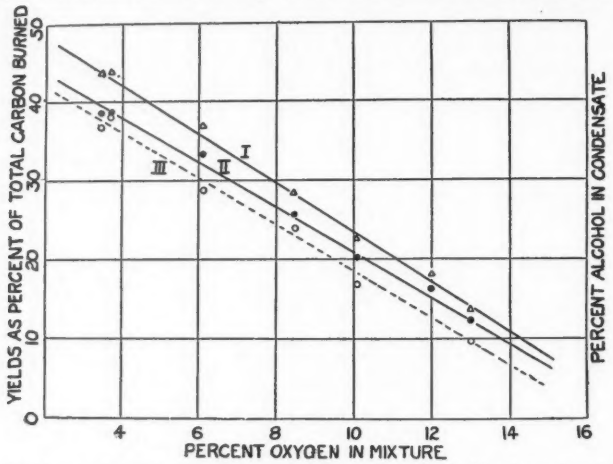

FIG. 3. *Yields as a function of oxygen concentration, from Table II. I, total useful oxygen compounds; II, methanol; III, weight per cent methanol in liquid condensate.*

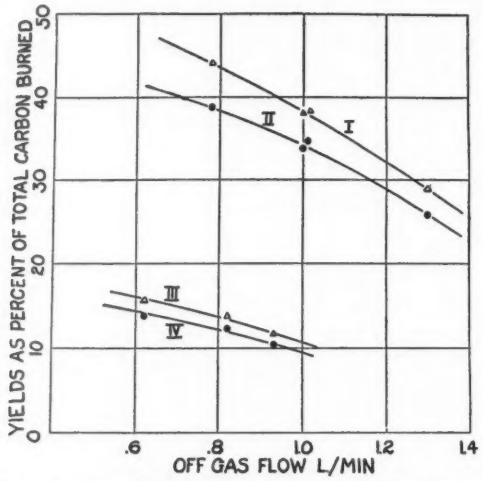

FIG. 4. *Yields as a function of off-gas flow, from Table III. I and II; total useful oxygen compounds and methanol respectively at a low oxygen concentration; III and IV, the same at a high oxygen concentration.*

The relation between the amount of carbon oxidized and the oxygen concentration can be seen by inspection of Table II. A linear relation is, of course, obtained. The results are of interest chiefly from the practical point of view when taken in conjunction with Graph I of Fig. 3. Obviously the greatest consumption of carbon per pass is desired in practice, with as great an efficiency of conversion to useful products as possible. The two requirements are in opposition, however; as carbon oxidized increases from 4 to 8%, the yield drops from 45 to 30% with increasing oxygen concentration. The greatest yield of useful products, 2.9%, occurs when the oxygen concentration is about 10%, but only 22% of the carbon oxidized enters into the formation of useful products.

TABLE III

EXPERIMENTS AT 350° C. AND PRESSURES NEAR 185 ATM., SHOWING THE EFFECT OF RATE OF FLOW ON YIELDS FOR TWO OXYGEN CONCENTRATIONS

Experiment No.	55	59	53	77	80	81	79
Pressure in atm.	188	182	168	185	188	185	188
Off-gas flow, litres per min.	0.62	0.82	0.93	0.78	1.0	1.04	1.30
In-gas analysis							
O_2	12.68	13.2	12.9	3.76	3.68	3.66	3.73
CH_4	35.56	33.4	34.9	76.4	75.3	75.4	75.3
C_2H_6	1.19	1.1	1.15	1.88	2.42	2.63	2.66
N_2	50.57	52.3	51.05	17.96	18.6	18.31	18.31
Off-gas analysis							
CO_2	3.6	3.52	3.0	0.61	1.07	0.95	2.45
O_2	0.7	0.52	0.3	0.32	0.21	0.21	0.5
H_2	0.8	1.03	2.7	0.47	0.42	0.53	0.5
CO	2.9	1.97	4.3	1.21	1.08	1.24	1.21
CH_4	36.4	34.2	33.8	77.8	78.5	77.6	75.0
C_2H_6	0.2	0.63	0.2	1.1	0.81	1.5	1.48
N_2	55.4	58.13	55.7	18.49	17.9	17.97	18.86
Volume in-gas / Volume off-gas	1.17	1.17	1.14	1.04	1.04	1.04	1.03
Condensate, gm. per 100 l. in-gas at N.T.P.							
CH_3OH	1.30	0.96	1.06	1.73	1.60	1.72	1.83
CH_2O	0.127	0.101	0.103	0.198	0.166	0.151	0.185
HCOOH	0.014	0.011	0.016	0.031	0.037	0.040	0.033
H_2O	9.79	8.73	9.88	2.46	2.76	2.35	2.11
Alcohol in condensate, %	11.6	9.82	9.58	39.0	35.1	40.3	44.0
Total carbon oxidized, %	17.3	15.3	19.5	3.92	4.16	4.31	6.17
Yields, as % of total carbon burned to:							
CH_3OH	13.9	12.34	10.3	38.8	33.8	34.6	25.8
CH_2O	1.44	1.39	1.06	4.75	3.72	3.25	2.77
HCOOH	0.11	0.1	0.1	0.48	0.54	0.57	0.32
Total	15.45	13.73	11.46	44.03	38.06	38.32	28.9
Total inlet oxygen accounted for, %	92.2	81.5	88.4	99.0	111.0	105.0	146.0

Effect of Rate of Flow

Some data illustrating the effect of rate of flow of the gas mixture over the catalyst are given in Table III and illustrated in Fig. 4. The change in yield with increasing rate of flow is in the same direction for both oxygen concentrations. Within the limits investigated, the yield falls off slowly with increasing rate of flow. This, of course, is only to be expected, and it might be predicted that at lower rates of flow than those used, a falling-off in yield would occur also. Thus, an optimum rate of flow resulting in maximum yield could be found somewhat lower than the lowest rate used. The other products of the experiments behave in a manner to be expected with changing yield of useful products.

Effect of Temperature

The effect of temperature at two different oxygen concentrations is shown by the data of Table IV. The data of Experiments 53, 56, and 57, in which 12.7% oxygen was used, show clearly a decrease in yield with increasing temperature, a 50% decrease for a 50° C. rise. Production of water increased, as did that of carbon monoxide and hydrogen in the off-gas. The apparent survival of ethane at the higher temperatures may not be real. The amounts are small and almost within experimental error, but the observation is emphasized because of its relation to other experiments.

The data of Experiments 85 to 93, in which a lower oxygen concentration was used, show no clearly marked trend with temperature. The yields are higher than those obtained in similar experiments the results of which are given in Table II (compare No. 77 with 93), and suggest an improvement in the catalyst with age. A poisoning action, which may be suspected in the experiments of Table II, will be discussed later.

It is interesting to notice the survival of ethane in all the experiments of Table IV at the lower oxygen concentration, and possibly an increase in ethane at the higher temperatures. This is contrary to what might be expected, since ethane is less stable than methane. The results of duplicate experiments were erratic, but there was no doubt as to the occurrence of hydrocarbons higher than methane. At 425° C. unknown gaseous compounds appeared in the off-gas. These compounds were hydrocarbons, insoluble in fuming sulphuric acid but oxidized by hot copper oxide. They interfered with the hydrogen and carbon monoxide determinations and consequently material balances could not be made. One experiment, No. 91, is included, and the yields are good.

Poisoning of the Catalyst

Some experiments illustrating loss of activity of the copper catalyst are given in Table V. Experiments 62, 63, and 64 may be compared with similar experiments the results of which are given in Table II, namely, Nos. 66, 67, and 76 or 77. Poisoning was very evident and could easily be detected, without going through all the analytical procedure, by the greater heat input to the reactor. It was due invariably to failure of the purification system, with

TABLE IV

EXPERIMENTS AT PRESSURES NEAR 185 ATM. AND RATES OF FLOW NEAR 1.0 LITRE PER MIN. SHOWING THE EFFECT OF TEMPERATURE ON YIELDS FOR TWO OXYGEN CONCENTRATIONS

Experiment No.	57	53	56	92	86	87	93	88	85	91
Temperature, °C.	325	350	375	325	325	325	350	350	400	425
Pressure in atm.	180	168	178	185	185	185	185	186	185	185
Off-gas flow, litres per min.	0.8	0.93	0.86	0.9	0.95	1.0	0.94	1.08	0.94	1.00
In-gas analysis										
O_2	12.7	12.9	12.5	3.98	4.1	3.89	4.22	3.63	3.71	3.68
CH_4	35.7	34.9	36.4	73.65	72.2	74.7	72.35	77.1	73.8	77.1
C_2H_6	1.2	1.15	1.2	2.73	2.76	2.14	3.20	2.61	2.03	2.0
N_2	50.4	51.05	49.9	19.64	20.94	19.27	20.23	17.24	19.88	17.2
Off-gas analysis										
CO_2	3.0	3.0	2.6	0.63	0.58	0.58	0.74	0.47	0.53	0.42
O_2	2.6	0.3	0.6	0.39	0.0	0.19	0.21	0.19	0.0	0.0
H_2	1.3	2.7	2.4	0.47	0.63	0.50	0.37	0.56	0.53	–
CO	2.5	4.3	5.5	0.14	0.63	0.72	0.21	0.63	0.53	–
CH_4	37.7	33.8	34.3	74.6	74.9	75.8	73.1	78.75	75.1	–
C_2H_6	0.0	0.2	0.3	2.53	1.81	2.01	3.45	1.79	2.68	–
N_2	52.9	55.7	54.3	21.24	21.45	20.2	21.92	17.61	20.63	–
Volume in-gas / Volume off-gas	1.16	1.14	1.09	1.03	1.03	1.02	1.05	1.05	1.05	1.00
Condensate, gm. per 100 l. in gas at N.T.P.										
CH_3OH	0.953	1.06	0.695	1.70	2.20	2.12	1.80	1.83	1.97	2.06
CH_2O	0.153	0.103	0.093	0.147	0.194	0.187	0.153	0.224	0.198	0.094
HCOOH	0.008	0.016	0.024	0.026	0.063	0.057	0.0	0.028	0.02	0.01
H_2O	8.78	9.88	12.66	2.53	2.90	2.70	2.70	2.12	2.66	3.15
Alcohol in condensate, %	9.62	9.58	5.16	38.6	41.0	41.9	38.7	43.4	40.6	38.8
Total carbon oxidized, %	14.7	19.5	20.6	2.6	3.73	3.72	2.90	3.10	3.24	–
Yields, as % of total carbon burned to:										
CH_3OH	12.0	10.3	6.1	58.0	53.3	51.0	55.5	51.0	54.3	–
CH_2O	2.04	1.06	0.86	5.53	5.02	4.77	5.0	6.65	5.75	–
HCOOH	0.143	0.1	0.14	0.62	1.06	0.95	0.0	0.54	0.37	–
Total	14.2	11.46	7.10	64.15	59.38	56.72	60.5	58.19	60.42	–
Total inlet oxygen accounted for, %	93.0	88.4	107.0	78.5	87.0	88.6	81.0	83.0	87.0	–

consequent introduction of sulphur or the admission of heavy oils and vapors. Generally, the system was cleaned thoroughly and the catalyst washed with dilute nitric acid to clear up the trouble. Mere traces of poisons difficult to detect, other than by means of the effect on the catalyst, were sufficient to reduce catalytic activity.

The remaining experiments in Table V illustrate the abrupt poisoning of the catalyst and its slow regeneration. This was shown by letting the reactions take place over a long period of time. The period was divided into three experiments, Nos. 73, 74, and 75. The catalyst was poisoned by sulphur in

TABLE V

EXPERIMENTS AT 350° AND 185° C., SHOWING THE EFFECTS OF POISONING THE CATALYST AT TWO OXYGEN CONCENTRATIONS

Experiment No.	72	73	74	75	62	63	64
Off-gas flow, litres per min.	0.87	0.68	0.79	0.71	0.76	0.77	0.98
In-gas analysis							
O_2	3.95	3.82	3.80	3.69	6.81	8.62	3.53
CH_4	74.8	74.7	75.5	75.7	61.0	53.3	76.7
C_2H_6	2.05	2.24	2.0	1.93	2.02	1.76	1.93
N_2	19.2	19.24	18.62	18.68	30.17	36.33	17.6
Off-gas analysis							
CO_2	1.92	1.40	0.84	0.74	1.86	2.16	1.16
O_2	0.34	0.32	0.38	0.53	0.52	0.84	0.42
H_2	0.42	0.35	0.42	0.37	0.31	0.63	0.21
CO	0.85	0.84	1.35	1.27	1.67	2.27	0.79
CH_4	76.7	77.6	77.7	76.7	66.0	53.8	79.5
C_2H_6	1.40	1.39	0.97	1.1	0.80	0.70	0.54
N_2	18.37	18.10	18.34	19.29	28.8	39.6	18.2
Volume in-gas / Volume off-gas	1.06	1.06	1.05	1.03	1.11	1.07	1.03
Condensate, gm. per l. in-gas at N.T.P.							
CH_3OH	1.09	1.30	1.68	1.64	1.29	1.13	0.654
CH_2O	0.144	0.156	0.18	0.175	0.201	0.173	0.145
HCOOH	0.019	0.023	0.032	0.033	0.035	0.034	0.026
H_2O	2.58	2.40	2.31	2.21	6.64	7.95	3.25
Alcohol in condensate, %	28.6	33.5	40.0	40.3	15.8	12.1	16.0
Total carbon oxidized, %	4.45	4.0	4.3	4.07	6.52	8.96	3.07
Yields, as % of total carbon burned to:							
CH_3OH	22.0	29.0	34.5	35.6	21.4	15.5	18.6
CH_2O	3.06	3.7	3.94	4.03	3.55	2.55	4.4
HCOOH	0.26	0.35	0.45	0.5	0.32	0.40	0.51
Total	25.32	33.05	39.0	40.13	25.35	18.37	23.54
Total oxygen accounted for, %	116.0	106.0	102.7	105.0	98.2	108	120

Experiment 72, and the purification system was overhauled immediately. With continued use, an improvement in the activity of the catalyst took place. The rate of improvement fell off greatly, however, and normal activity, as in No. 77, Table II, was obtained only after the reaction system and catalyst had been cleaned.

The sensitivity of copper to poisons is a serious disadvantage from the practical point of view. Most natural gases contain sulphur, and its complete removal is difficult. A less sensitive catalyst or a method of operation that eliminates poisoning is highly desirable, and some attention has been given the matter in later work.

Conclusions

It may be concluded that the yield of useful products depends primarily on the catalyst, the oxygen concentration, and the temperature. The influence of the time of reaction and the pressure, within the limits studied, is small. The catalyst chosen, copper, fulfils at least two functions in providing a metallic surface easily oxidized and reduced, and in aiding in the dissipation of the heat of reaction. Gas phase reactions and lack of temperature control are both detrimental. This suggests that the desired reactions take place on surfaces and are highly sensitive.

The general features of the results may be explained reasonably well on the basis of the "hydroxylation theory" (1). Obvious confirmation of the theory lies in the production of large amounts of methanol and small amounts of formaldehyde and formic acid when the oxidation of methane is carried out under pressure. The dependence of yield on oxygen concentration, or, in another way, the requirement of a large oxygen deficiency for high conversion to methanol, is also explicable on the basis of the theory. Finally, many tests on the liquid and gaseous products of the reactions for peroxides were negative.

A great many details remain, however, unexplained. Reference is to the minor products and the kinetics of the reactions. It is believed that the chain mechanism advanced by Norrish (4) offers some help in this connection. Further experimental data are necessary, however, and will be presented together with a discussion in a later report.

References

1. Bone, W. A. Proc. Roy. Soc. (London), 134 A : 243-274. 1932.
2. Boomer, E. H. and Broughton, J. W. Can. J. Research, B, 15 : 375-382. 1937.
3. Boomer, E. H. and Johnson, C. A. Can. J. Research, B, 15 : 363-366. 1937.
4. Norrish, R. G. W. Proc. Roy. Soc. (London) 150 A : 36-57. 1935.
5. Wiezevitch, P. J. and Frolich, P. K. Ind. Eng. Chem. 26 : 267-276. 1934.

THE OXIDATION OF METHANE AT HIGH PRESSURES

III. EXPERIMENTS USING PURE METHANE AND PRINCIPALLY COPPER AS CATALYST[1]

By E. H. Boomer[2] and V. Thomas[3]

Abstract

Mixtures of methane containing some nitrogen and oxygen were passed over copper and silver catalysts. The effects of the variables, composition of mixture, pressure, and temperature were determined. From 3 to 7% of oxygen was used in various experiments at pressures from 140 to 220 atm. at a temperature of 475° C. The effect on yields of additions of carbon dioxide to the mixture was determined.

Introduction

Previous reports have described preliminary experiments (2) and a systematic investigation (4) on the oxidation by air of a natural gas of high methane content. The present report deals with experiments on methane, in which principally copper was used as catalyst, but including some work with other catalysts.

In earlier work, the presence of ethane and higher hydrocarbons in the natural gas used resulted in some ambiguity with regard to the results. It was impossible to decide just how much of the products of the reaction was due to methane and how much due to other hydrocarbons. In order to obtain a definite knowledge of the reactions taking place, the present series of experiments were carried out using a gas mixture, containing only methane, oxygen, and nitrogen. In the systematic investigations on the effect of variables such as pressure, temperature, composition, and rate of flow of gas, copper was used as catalyst. In addition some experiments were carried out with other catalysts.

Experimental

The experimental methods differed in some details from those described in previous reports. The difference was principally in the preparation of gas mixtures and control of pressures in the apparatus.

Materials

Natural gas from the Viking field near Edmonton was used as a source of methane. The higher hydrocarbons were removed by a method of pyrolysis followed by elimination of the products of pyrolysis which has been described (3). The gas had the composition by volume: methane, 94.3; nitrogen, 5.7%. Air was used as oxidant after drying over calcium chloride and removal of carbon dioxide with solid potassium hydroxide.

[1] *Manuscript received May 31, 1937.*
Contribution from the Chemical Laboratories, University of Alberta, Edmonton, Canada, with financial assistance from the Carnegie Corporation Research Grant to the University of Alberta and equipment provided by the National Research Council of Canada and the Research Council of Alberta.

[2] *Associate Professor of Chemistry, University of Alberta.*
[3] *Research Assistant, Carnegie Corporation Research Grant to the University of Alberta, 1935-1936.*

The catalysts used were copper, silver, a high nickel-chromium steel (Enduro KA2S), and glass. The copper catalyst was cut into $\frac{3}{16}$ in. squares, $\frac{3}{32}$ in. thick. It weighed 39.8 gm. and its volume was 4.46 cc. The silver catalyst was in the form of $\frac{3}{16}$ in. squares cut from 0.004 in. sheet. It weighed 15.35 gm. and its volume was 1.46 cc. The steel catalyst, in the form of machine turnings about 6 mesh in size, weighed 17.13 gm. and had a volume of 2.20 cc. The glass catalyst consisted of $\frac{3}{8}$ in. lengths of $\frac{1}{8}$ in. soft glass tubing. It weighed 8.16 gm. All catalysts occupied about the same space; namely, 12 cc. when packed in the reactor.

Apparatus

In these experiments the supply of methane was limited and only a small storage cylinder was used. In order to prevent a large pressure drop during the reaction, a storage and pressure control system as shown in Fig. 1. was

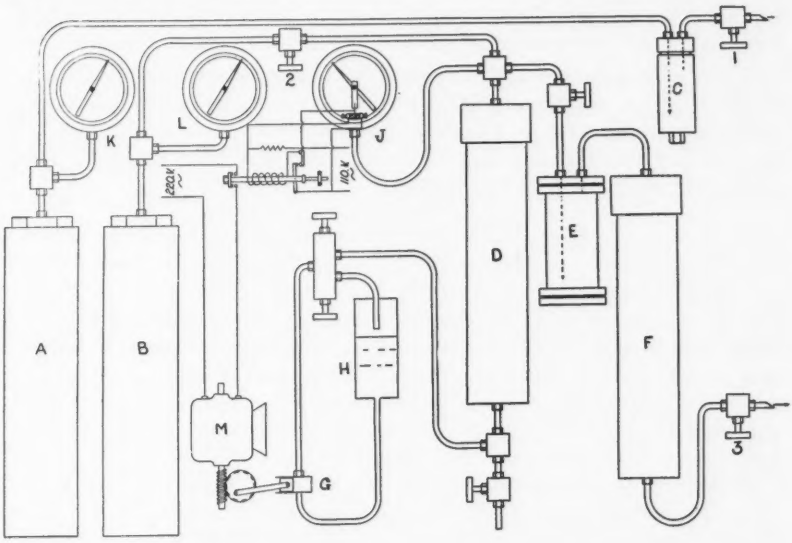

FIG. 1. *Apparatus for automatic control of high gas pressures.*

devised. Large cylinders, *A* and *B*, contained air and methane respectively. The air storage pressure was some 35 atm. greater than the pressure to be used in an experiment, and the cylinder was of such size that the pressure dropped only a few atmospheres during the course of an experiment. Methane was taken from cylinder *B* to the hydraulic cylinder, *D*, and subsidiary storage cylinder, *F*. A hydraulic pump, *G*, was used to pump a 50% glycerine-water mixture into cylinder *D* until the pressure was equal to the experimental value required. Two contacts, high and low, on the pressure gauge, *J*, operating through a relay (G.E., 2904 G2) controlled the motor, *M*. As gas

was withdrawn through valve 3 to the reaction system, the movement of the gauge index operated the motor, and this resulted in entry of fluid to cylinder *D*, and a constant pressure. The system was sensitive to a pressure drop of less than one atmosphere, hardly discernible on the gauge.

The pressure bottle *C* contained solid potassium hydroxide, and valve 1 was connected through a check valve to the air control valve on the reaction system. The pressure bottle *E* contained, in order, calcium chloride and activated coconut charcoal to give the methane a final purification. Valve 3 was connected through a check valve to the gas control valve on the reaction system.

The reaction system and its operation has been described in detail (4), and does not require discussion except in one regard—the operating procedure is different. In the present case, the gas valve was opened and the system brought to the operating pressure as maintained by the control described above. The air valve was then opened and adjusted until the composition of the gas-air mixture was that desired as shown by the thermal conductivity analyses.

The analytical procedure followed with regard to the gas mixtures and products of the reaction, as well as occasional confirmations by ultimate analysis, was the same as that described previously (4). All analyses were made in duplicate and any doubtful results resulted in rejection of the experiment unless checks could be obtained.

Experimental Results

The results are presented in the form of tables giving the essential data and graphs illustrating salient features of the data. In all cases, the element carbon has been taken as the reference substance, and calculations of material balances have been made upon that basis. No evidence was ever obtained that carbon was lost in the apparatus or in the products in appreciable amounts, and, furthermore, the nitrogen balance was in general agreement with the carbon balance. The hydrogen balance showed greater and erratic errors but of no great significance. However, the oxygen balance, on the assumption that the carbon balance was correct, was greatly in error. There was invariably a loss of oxygen which was, except rarely, greater than any conceivable error of analysis, and it has not yet been possible to explain the loss in any reasonable manner. The same result was obtained previously (4), although not so consistently, and has been noticed elsewhere (6).

A result of some importance and interest was found immediately these experiments were begun. Temperatures of at least 350° C. were necessary to initiate oxidation of methane, and temperatures higher than 400° C. were the most satisfactory. The range 425° to 475° C. was found to produce the highest yields and was, as a consequence, generally used. The much lower temperatures (4) required with Viking natural gas may be attributed to the ethane and propane present. These gases would oxidize at a lower temperature than would methane, and possibly stimulate the oxidation of the more resistant methane.

Effect of Oxygen Concentration on Yields

Experiments showing the effect of oxygen concentration in the gas mixture on the yields of useful products at three different pressures are given in Tables I, II, and III. Figs. 2 and 3 illustrate graphically these results. The reactions were very similar in behavior at all pressures, showing a rapid decrease in yield with increasing oxygen concentration. The graphs of Fig. 2 are curved and show a rapid increase in slope at high oxygen concentrations, a result that may be compared with the straight lines obtained when Viking natural gas (4) is used in place of methane. Another comparison is given in Fig. 3. Here, the straight lines I and II have been taken from the data on natural gas. The graphs for methane show a curvature and a maximum in the region of 6% oxygen. It is of interest to note that this point of maximum consumption of carbon corresponds to the oxygen concentration at which the yields begin to fall off rapidly.

TABLE I

EXPERIMENTS WITH DIFFERENT OXYGEN CONCENTRATIONS CARRIED OUT AT 475° C. AND 141 ATM. PRESSURE

Experiment No.	154	153	155	156
Off-gas flow, litres/min.	0.89	0.90	0.89	0.84
In-gas analysis:				
O_2	2.77	4.42	6.32	8.35
CH_4	81.6	74.3	65.7	56.6
N_2	15.63	21.28	27.98	35.05
Off-gas analysis:				
CO_2	0.53	0.79	1.05	1.23
O_2	0.0	0.13	0.11	0.0
H_2	0.55	0.63	1.29	0.63
CO	0.0	0.0	0.24	0.0
CH_4	84.15	76.8	68.6	59.1
N_2	14.77	21.65	28.71	39.04
$\frac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.05	1.04	1.09	1.08
Condensate, gm./100 litres in-gas at N.T.P.				
Total	2.69	4.29	6.32	8.43
CH_3OH	1.01	1.30	1.35	0.778
CH_2O	0.0657	0.075	0.10	0.0973
HCOOH	0.0246	0.0409	0.0423	0.0477
H_2O	1.59	2.87	4.83	7.51
Alcohol in condensate, %	37.6	30.3	21.3	9.22
Total carbon oxidized, %	1.57	2.43	3.40	3.16
Yields, as % of total carbon burned to:				
CH_3OH	55.7	54.0	42.2	30.6
CH_2O	3.80	3.12	3.36	4.07
HCOOH	0.94	1.12	0.93	1.26
Total	60.44	58.24	46.49	35.93
Total inlet oxygen accounted for, %	68.0	71.8	74.5	80.5

A similar, though not pronounced, difference exists with regard to the concentration of alcohol in the condensate. Instead of showing a linear relation a curve is obtained showing a greater slope at higher oxygen concentrations.

No definite conclusions can be drawn with regard to the minor constituents of the off-gases. Possibly the observation of most interest was the absence of carbon monoxide in the products obtained at lower oxygen concentrations. This was generally true in all experiments with methane. It is significant of the effect of higher hydrocarbons that, in all experiments with natural gas, carbon monoxide was a product. Another significant feature that was observed was the formation of traces of higher hydrocarbons in all experiments with methane. The amounts were small and within the experimental error; they have not been listed. However, they were found consistently and it appeared that the amounts were greater at higher oxygen concentrations. The occurrence, to be discussed later, of traces of oils among the liquid products may be related to the above observation.

TABLE II

EXPERIMENTS WITH DIFFERENT OXYGEN CONCENTRATIONS CARRIED OUT AT 475° C. AND 184 ATM. PRESSURE

Experiment No.	115	99	116	117	118	119	137
Off-gas flow, litres/min.	0.84	0.80	0.81	0.77	0.83	0.79	0.78
In-gas analysis:							
O_2	3.22	4.85	5.53	6.93	7.0	7.9	8.63
CH_4	80.0	72.5	69.1	63.0	62.7	56.9	55.4
N_2	16.78	22.65	25.37	30.07	30.3	35.2	35.97
Off-gas analysis:							
CO_2	0.34	0.58	0.63	0.87	0.95	0.97	1.37
O_2	0.16	0.47	0.32	0.32	0.13	0.24	0.13
H_2	0.26	0.26	0.37	0.45	0.05	0.58	1.84
CO	0.0	0.0	0.0	0.0	0.0	0.11	0.21
CH_4	81.4	74.9	72.9	66.4	66.6	61.5	58.6
N_2	17.84	23.79	25.78	31.96	32.27	36.6	37.85
Volume in-gas / Volume off-gas	1.04	1.04	1.09	1.08	1.09	1.11	1.10
Condensate, gm./100 litres in-gas at N.T.P.							
Total	3.78	5.05	5.44	6.27	6.43	4.88	8.05
CH_3OH	1.60	1.66	1.57	1.15	1.27	0.69	0.621
CH_2O	0.078	0.051	0.077	0.07	0.081	0.079	0.076
HCOOH	0.0304	0.0441	0.0314	0.0306	0.0324	0.0249	0.0244
H_2O	2.07	3.30	3.75	5.02	5.05	4.09	7.33
Alcohol in condensate, %	42.2	32.9	29.0	18.5	19.7	14.1	7.72
Total carbon oxidized, %	1.90	2.48	2.54	2.66	2.90	2.70	3.52
Yields, as % of total carbon burned to:							
CH_3OH	74.0	65.3	62.8	48.2	49.2	31.6	22.4
CH_2O	3.82	2.16	3.28	3.12	2.16	3.84	2.94
HCOOH	0.98	1.20	0.87	0.91	0.86	0.90	0.62
Total	78.8	68.66	66.95	52.23	52.22	36.34	25.96
Total inlet oxygen accounted for, %	73.6	76.3	69.0	67.6	66.4	50.4	73.0

The Effect of Pressure on Yields

The effect of pressure may be seen from a study of Tables I, II, and III and Fig. 2. Over most of the range of oxygen concentrations, the yield passed through a maximum as the pressure was raised from 141 to 231 atm. The yield at 184 atm. was greater than that at the lower and higher pressures. However, at a concentration of 7% of oxygen the graphs begin to cross, and ultimately the highest yield is obtained at a pressure of 141 atm. At these high oxygen concentrations the yields were very low and the experiments difficult to control. Little weight can be placed on the results, and it might be said that pressure had little or no effect at high oxygen concentrations. However, there was no doubt as to the reality of the effect at low oxygen concentrations, an effect explicable only when the kinetics of the reactions is known.

TABLE III

EXPERIMENTS WITH DIFFERENT OXYGEN CONCENTRATIONS CARRIED OUT AT 475° C. AND 231 ATM. PRESSURE

Experiment No.	151	146	144	143
Off-gas flow, litres/min.	0.84	0.84	0.84	0.84
In-gas analysis:				
O_2	3.18	4.42	6.73	8.74
CH_4	79.8	74.3	63.9	54.9
N_2	17.02	21.28	29.37	36.36
Off-gas analysis:				
CO_2	0.53	0.63	1.05	1.26
O_2	0.0	0.05	0.16	0.13
H_2	0.5	0.55	1.55	2.03
CO	0.0	0.0	0.11	0.34
CH_4	82.5	77.5	67.2	38.0
N_2	16.47	21.27	29.93	38.24
$\frac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.05	1.06	1.09	1.09
Condensate, gm./100 litres in-gas at N.T.P.				
Total	3.26	4.81	6.61	8.20
CH_3OH	1.34	1.67	1.54	0.694
CH_2O	0.0604	0.0833	0.0965	0.0633
HCOOH	0.0195	0.0447	0.0435	0.0523
H_2O	1.84	3.02	4.93	7.40
Alcohol in condensate, %	41.0	34.9	23.3	8.46
Total carbon oxidized, %	1.87	2.49	3.48	3.67
Yields, as % of total carbon burned to:				
CH_3OH	62.7	63.2	48.6	24.2
CH_2O	3.03	3.36	3.24	2.30
HCOOH	0.63	1.18	0.95	1.25
Total	66.36	67.74	52.8	27.75
Total inlet oxygen accounted for, %	67.7	72.2	73.0	72.5

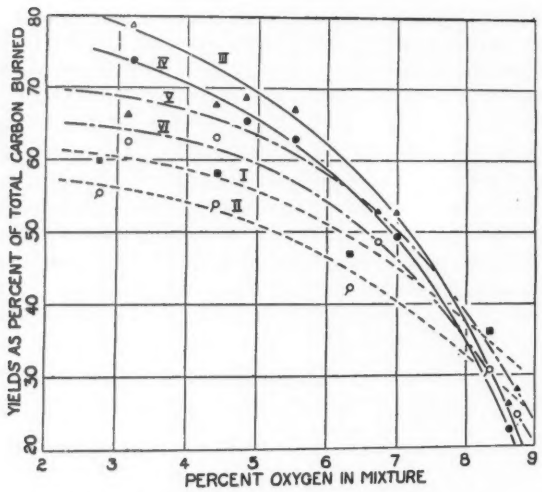

FIG. 2. *Yields as a function of oxygen concentration and pressure, from Tables I, II, and III. I, III, and V; total useful oxygen compounds at 141, 184, and 231 atm. respectively: II, IV, and VI; methanol at the same pressures.*

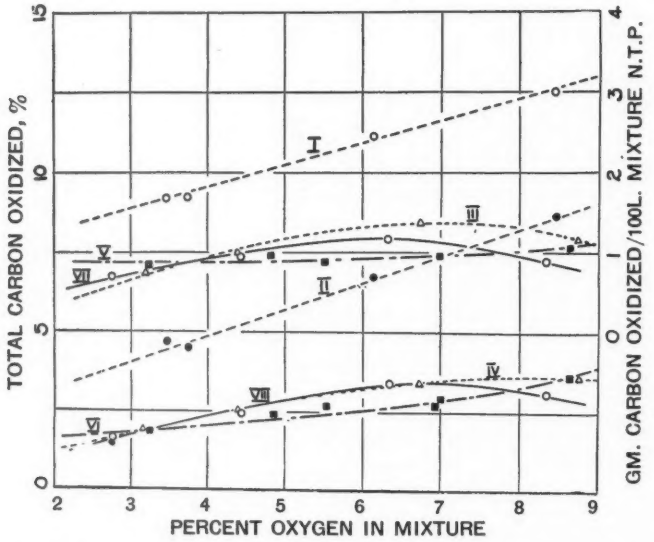

FIG. 3. *Carbon oxidized as a function of oxygen concentration and pressure, from Tables I, II, and III. Even numbered curves, per cent, odd numbered curves, grams. I and II, natural gas; III and IV, V and VI, VII and VIII, for 141, 184, and 231 atm. pressure respectively.*

Effect of Temperature on Yields

A considerable number of experiments were carried out under various conditions to determine the effect of different temperatures on yields. The results are given in Tables IV, V, VI, and VII, and illustrated in Figs. 4 and 5. The data of Tables V and VII are shown in Fig. 4, and give the results for two pressures at low oxygen concentrations. Obviously there is an optimum temperature around 450° C. which is the same for both pressures. It was interesting to note during these experiments that control of the reactions was much easier at temperatures higher than 400° C. than below.

TABLE IV

EXPERIMENTS AT DIFFERENT TEMPERATURES AND 231 ATM. PRESSURE, USING ABOUT 8.7% OF OXYGEN

Experiment No.	140	139	138	142	143
Temperature, °C.	360	390	390	425	475
Off-gas flow, litres/min.	0.79	0.80	0.93	0.80	0.84
In-gas analysis:					
O_2	8.74	8.54	8.30	8.74	8.74
CH_4	54.9	55.8	56.7	54.9	54.9
N_2	36.36	35.66	35.0	36.36	36.36
Off-gas analysis:					
CO_2	2.28	2.08	2.16	1.68	1 26
O_2	0.47	0.16	0.13	0.26	0.13
H_2	0.47	0.63	0.61	1.34	2.03
CO	0.0	0.16	0.10	0.20	0.34
CH_4	58.7	58.7	59.35	58.4	58.0
N_2	38.08	38.27	37.65	38.03	38.24
$\frac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.14	1.12	1.11	1.12	1.09
Condensate, gm./100 litres in-gas at N.T P.					
Total	8.55	8.69	8.44	8.39	8.20
CH_3OH	1.74	1.91	1.85	1.37	0.694
CH_2O	0.116	0.114	0.104	0.0908	0.0633
HCOOH	0.0707	0.0407	0.0411	0.0596	0.0523
H_2O	6.63	6.63	6.43	6.87	7.40
Alcohol in condensate, %	20.4	22.0	21.9	16.4	8.46
Total carbon oxidized, %	6.13	6.18	6.05	5.13	3.67
Yields, as % of total carbon burned to:					
CH_3OH	37.0	38.8	37.8	34.2	24.2
CH_2O	2.58	2.48	2.26	2.42	2.30
HCOOH	1.03	0.58	0.59	1.03	1.25
Total	41.61	41.86	40.65	37.65	27.75
Total inlet oxygen accounted for, %	82.8	81.0	82.2	76.5	72.5

The stability of the copper catalyst as regards temperature was demonstrated by these experiments. Between Experiments 94 and 101, Table VII, the temperature was varied from 350° to 500° C. without any intermediate activations, and yet the two experiments agreed well with each other.

The data of Tables IV and VI, shown graphically in Fig. 5, give the effect of temperature at two pressures and high oxygen concentrations. The optimum temperature was lowered to 390°C. by increasing the oxygen concentration, but it was still nearly independent of pressure.

TABLE V

EXPERIMENTS AT DIFFERENT TEMPERATURES AND 231 ATM. PRESSURE, USING ABOUT 4.4% OF OXYGEN

Experiment No.	149	150	147	145	146	148
Temperature, °C.	390	425	425	475	475	506
Off-gas flow, litres/min.	0.90	0.84	0.88	0.86	0.84	0.87
In-gas analysis:						
O_2	4.28	4.48	4.42	4 42	4.42	4.42
CH_4	74.8	73.8	74.3	74.3	74.3	74.3
N_2	20.92	21.72	21.28	21.28	21.28	21.28
Off-gas analysis:						
CO_2	0.84	0.79	0.83	0.73	0.63	0.73
O_2	0.0	0.11	0.0	0.13	0.05	0.05
H_2	0.37	0.50	0.53	0.89	0.55	0.82
CO	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	77.8	77.8	77.4	77.2	77.5	77.1
N_2	20.99	20.8	21.24	21.02	21.27	21.3
Volume in-gas / Volume off-gas	1.06	1.08	1.06	1.07	1.06	1.06
Condensate, gm./100 litres in-gas at N.T.P.						
Total	4.84	4.73	4.79	4.70	4.81	4.48
CH_3OH	1.74	1.72	1.63	1.66	1.67	1.42
CH_2O	0.109	0.081	0.078	0.0743	0.0833	0.0769
HCOOH	0.0273	0.026	0.0412	0.0454	0.0447	0.0361
H_2O	2.96	2.90	3.04	2.92	3.02	2.94
Alcohol in condensate, %	35.8	36.4	34.0	35.3	34.9	31.8
Total carbon oxidized, %	2.81	2.75	2.70	2.61	2.49	2.39
Yields, as % of total carbon burned to:						
CH_3OH	58.0	60.2	57.2	60.4	63.2	56.3
CH_2O	3.85	3.02	2.91	3.16	3.36	3.24
HCOOH	0.62	0.63	0.99	1.15	1.18	0.99
Total	62.47	63.85	61.10	64.71	67.64	60.53
Total inlet oxygen accounted for, %	77.8	73.2	73.3	74.5	72.2	73.0

The weight and composition of the liquid condensate did not vary greatly with temperature, the variation in yield being accounted for by variations in the amount of carbon oxidized. However, at the higher oxygen concentrations, the alcohol content paralleled the yield roughly. The changes in the composition of the off-gas were hardly significant except in one regard. As has been noted before, no carbon monoxide was found at any temperature with low oxygen concentrations, but was always present at high oxygen concentrations.

TABLE VI

EXPERIMENTS AT DIFFERENT TEMPERATURES AND 184 ATM. PRESSURE, USING ABOUT 8.7% OF OXYGEN

Experiment No.	126	135	130	133	132	136	137
Temperature, °C.	350	375	390	390	390	425	475
Off-gas flow, litres/min.	0.84	0.81	0.82	0.85	0.85	0.78	0.78
In-gas analysis:							
O_2	8.64	8.60	8.71	8.68	8.54	8.74	8.63
CH_4	55.4	55.5	55.0	55.2	55.8	54.9	55.4
N_2	35.96	35.9	36.29	36.12	35.66	36.36	35.97
Off-gas analysis:							
CO_2	2.00	2.42	2.09	2.52	2.52	1.79	1.37
O_2	0.11	0.11	0.05	—	0.11	0.21	0.13
H_2	1.16	0.58	0.82	0.61	0.71	1.16	1.84
CO	0.63	0.11	0.18	0.11	0.11	0.21	0.21
CH_4	58.55	57.9	59.1	58.3	58.1	58.0	58.6
N_2	37.55	38.88	37.76	38.46	38.45	38.63	37.85
Volume in-gas / Volume off-gas	1.10	1.11	1.11	1.13	1.11	1.11	1.10
Condensate, gm./100 litres in-gas at N.T.P.							
Total	8.53	8.27	8.75	8.34	8.35	8.39	8.05
CH_3OH	1.54	1.59	1.76	1.63	1.61	1.08	0.621
CH_2O	0.125	0.113	0.118	0.111	0.113	0.112	0.763
HCOOH	0.0388	0.0367	0.0432	0.0219	0.0306	0.0286	0.0244
H_2O	6.83	6.53	6.83	6.58	6.60	7.17	7.33
Alcohol in condensate, %	18.1	19.2	20.2	19.5	19.3	12.8	7.72
Total carbon oxidized, %	6.49	6.25	6.15	6.42	6.41	4.84	3.52
Yields, as % of total carbon burned to:							
CH_3OH	30.2	31.4	36.8	32.2	31.7	28.5	22.4
CH_2O	2.60	2.41	2.60	1.54	1.54	3.16	2.94
HCOOH	0.53	0.49	0.62	0.30	0.40	0.54	0.62
Total	33.3	34.3	40.02	34.04	33.64	32.2	25.96
Total inlet oxygen accounted for, %	81.7	81.6	80.0	81.0	83.7	79.2	73.0

TABLE VII

EXPERIMENTS AT DIFFERENT TEMPERATURES AND 184 ATM. PRESSURE, USING ABOUT 4.9% OF OXYGEN

Experiment No.	94	95	96	97	98	99	100	101
Temperature, °C.	350	375	400	425	450	475	500	350
Off-gas flow, litres/min.	0.73	0.70	0.78	0.66	0.79	0.80	0.74	0.74
In-gas analysis:								
O_2	4.86	4.96	5.03	4.85	4.85	4.85	4.85	4.85
CH_4	72.9	72.0	72.6	73.0	73.0	72.5	72.5	72.5
N_2	22.24	23.04	22.36	22.15	22.15	22.65	22.65	22.65
Off-gas analysis:								
CO_2	0.95	0.95	0.74	0.65	0.63	0.58	0.63	0.97
O_2	0.26	0.21	0.53	0.24	0.16	0.47	0.26	0.26
H_2	0.24	0.19	0.16	0.23	0.21	0.26	0.21	0.16
CO								
CH_4	75.45	74.8	74.2	75.4	75.5	74.9	75.2	75.3
N_2	23.1	23.85	24.37	23.48	23.39	23.79	23.7	23.31
Volume in-gas / Volume off gas	1.05	1.07	1.05	1.04	1.04	1.04	1.04	1.05
Condensate, gm./100 litres in-gas at N.T.P.								
Total	5.00	4.78	5.17	5.38	5.25	5.05	4.75	5.26
CH OH	1.67	1.57	1.73	1.82	1.76	1.66	1.40	1.74
CH_2O	0.134	0.115	0.158	0.139	0.0586	0.0508	0.0474	0.148
HCOOH	0.084	0.0726	0.0604	0.0814	0.0441	0.0441	0.0305	0.0505
H·O	3.12	3.02	3.22	3.34	3.39	3.30	3.27	3.32
Alcohol in condensate, %	33.3	32.9	33.4	33.9	33.6	32.9	29.6	33.1
Total carbon oxidized, %	3.03	2.93	2.85	2.80	2.61	2.48	2.26	3.14
Yields, as % of total carbon burned to:								
CH_3OH	52.7	52.2	58.8	62.5	65.1	65.3	60.2	53.4
CH_2O	4.53	4.08	5.07	5.07	2.26	2.16	2.16	4.85
HCOOH	1.85	1.67	1.42	1.94	1.12	1.20	0.93	1.08
Total	59.08	57.95	65.92	69.51	68.48	68.66	63.29	59.33
Total inlet oxygen accounted for, %	79.0	72.6	77.7	75.3	72.8	76.3	70.2	81.2

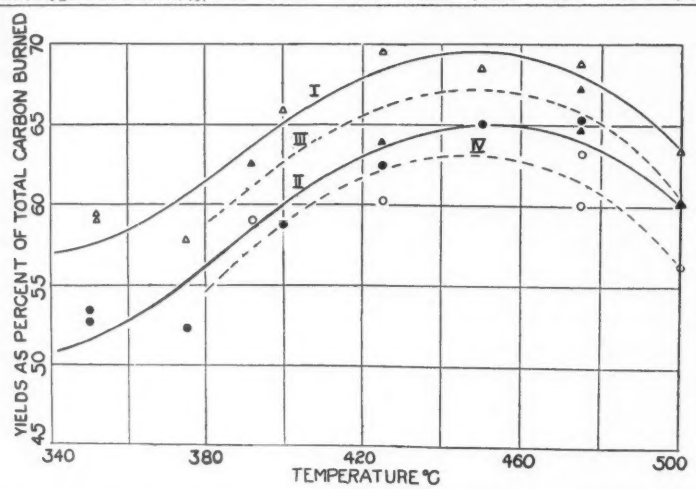

FIG 4. *Yields as a function of temperature, from Tables V and VII. I and II, total useful oxygen compounds and methanol respectively at 184 atm.; III and IV, the same at 231 atm.*

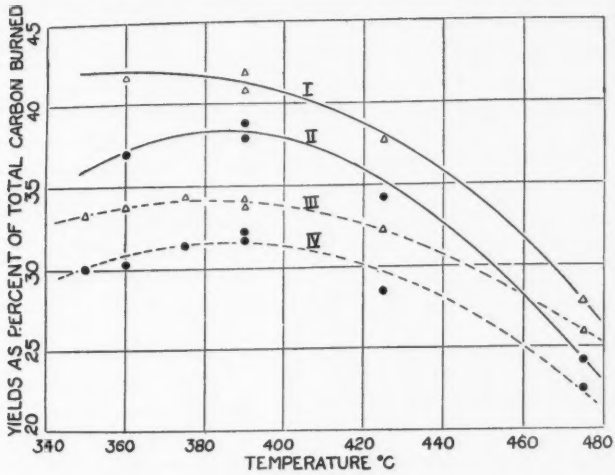

FIG. 5. *Yields as a function of temperature from Tables IV and VI. I and II, total useful oxygen compounds and methanol respectively at 184 atm.; III and IV, the same at 231 atm.*

TABLE VIII

EXPERIMENTS AT DIFFERENT RATES OF GAS FLOW AND 184 ATM. PRESSURE, USING ABOUT 4.9 AND 8.7% OF OXYGEN AT 475° AND 360° C. RESPECTIVELY

Experiment No.	108	99	110	111	125	134	127
Temperature, °C.	475	475	475	475	360	360	360
Off-gas flow, litres/min.	0.66	0.80	0.89	1.03	0.62	0.79	0.99
In-gas analysis:							
O_2	4.85	4.85	4.87	4.95	8.64	8.70	8.64
CH_4	72.7	72.5	72.7	72.3	55.4	55.0	55.4
N_2	22.45	22.65	22.43	22.75	35.96	36.3	35.96
Off-gas analysis:							
CO_2	0.63	0.58	0.53	0.63	2.16	2.52	1.92
O_2	0.31	0.47	0.21	0.16	0.32	0.11	0.16
H_2	0.11	0.26	0.26	0.11	0.71	0.68	1.16
CO	0.0	0.0	0.0	0.0	0.63	0.11	0.42
CH_4	75.0	74.9	75.5	75.2	58.1	58.1	59.5
N_2	23.95	23.79	23.5	23.8	38.08	38.48	36.84
Volume in-gas / Volume off-gas	1.05	1.04	1.05	1.06	1.10	1.13	1.11
Condensate, gm./100 litres in-gas at N.T.P.							
Total	5.06	5.05	5.25	5.28	8.71	7.95	8.48
CH_3OH	1.64	1.66	1.70	1.69	1.75	1.48	1.58
CH_2O	0.0472	0.0508	0.0607	0.0698	0.150	0.130	0.121
HCOOH	0.0404	0.0441	0.0337	0.0299	0.0479	0.0392	0.0463
H_2O	3.33	3.30	3.46	3.49	6.76	6.30	6.73
Alcohol in condensate, %	32.4	32.9	32.4	32.1	20.1	18.6	18.6
Total carbon oxidized, %	2.48	2.48	2.42	2.56	7.06	6.27	6.00
Yields, as % of total carbon burned to:							
CH_3OH	63.8	65.3	67.8	64.4	31.6	30.3	33.4
CH_2O	1.95	2.16	2.57	2.82	2.86	2.81	2.72
HCOOH	1.09	1.20	0.96	0.79	0.60	0.56	0.68
Total	66.84	68.66	71.33	68.01	35.06	33.67	36.8
Total inlet oxygen accounted for, %	74.0	76.3	72.0	72.0	86.3	79.5	79.6

Effect of Rate of Gas Flow on Yields

Table VIII and Fig. 6 show results illustrating changes in yield with rate of gas flow over the catalyst for two oxygen concentrations. The data are not particularly significant, especially at the higher oxygen concentration. A maximum appears in the graphs for low oxygen concentration and a minimum in the other case. A maximum might be expected, and would be observed more clearly no doubt if a wider range of gas flows had been used.

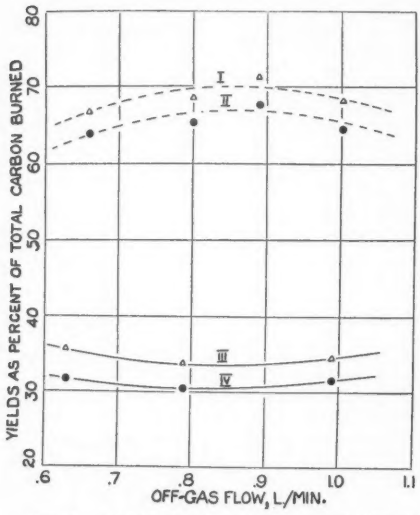

FIG. 6. *Yields as a function of rate of flow of off-gas, from Table VIII. I and II, total useful oxygen compounds and methanol respectively at a low oxygen concentration; III and IV, the same at a high oxygen concentration.*

Various Catalysts

Experiments in which the empty reactor and catalysts of glass, nickel-chromium steel, and silver were used are given in Table IX. The results of only two experiments in which the empty reactor was used are given, although a number were carried out. It was found difficult to obtain duplicates, the yield varying by about 50% in different experiments. Those listed are the experiments showing maximum yield. Because of the absence of any catalyst in the reactor, the free space was large, and the time that the gases were in the reactor was large. These conditions were shown to be unfavorable with natural gas (2), and the same conclusion may be drawn here. Good control evidently requires reasonable gas velocities and a small free space or large surface area or both. Experiments 159 and 161 may be compared to Experiments 156 and 153 of Table I in which copper was used. In this comparison it should be remembered that Experiments 159 and 161 were the most favorable of several, and the results could not be duplicated.

The experiments with glass and silver catalysts showed them to be as good as copper, a surprising result with glass at least. It was expected in view of the poor heat conductivity of glass that temperature control would be poor and the yields reduced. That glass was as good as copper may be seen by the results of Experiment 151 of Table II. It may be concluded that the reactions follow a different course over glass surfaces. Also, as an alternative, it may be suggested that reaction took place principally on the copper plated walls of the reactor, and the glass acted merely as a means of suppressing undesirable gas phase reactions.

TABLE IX

EXPERIMENTS USING THE EMPTY REACTOR AND CATALYSTS OTHER THAN COPPER AT 475° C.

Experiment No.	159	161	114	163	164
Catalyst			Glass	Steel	Silver
Pressure, atm.	141	141	184	141	141
Off-gas flow, litres/min.	0.84	0.88	0.85	0.88	0.89
In-gas analysis:					
O_2	8.68	4.53	3.16	4.42	4.22
CH_4	55.2	73.8	80.2	74.3	74.3
N_2	36.12	21.68	16.64	21.28	21.28
Off-gas analysis:					
CO_2	2.02	1.00	0.37	1.05	0.68
O_2	0.11	0.03	0.18	0.0	0.18
H_2	0.97	0.87	0.0	0.82	0.66
CO	0.11	0.0	0.0	0.0	0.05
CH_4	58.3	77.5	82.0	78.0	77.9
N_2	38.49	20.58	17.34	20.13	20.53
Volume in-gas / Volume off-gas	1.09	1.06	1.04	1.06	1.07
Condensate, gm./100 litres in-gas at N.T.P.					
Total	7.99	4.08	3.91	3.65	4.51
CH_3OH	1.23	1.20	1.71	1.03	1.25
CH_2O	0.0971	0.091	0.0644	0.0502	0.136
HCOOH	0.0586	0.0193	0.0305	0.0422	0.0254
H_2O	6.60	2.77	2.10	2.53	3.10
Alcohol in condensate, %	15.4	29.2	44.0	28.2	27.8
Total carbon oxidized, %	5.30	2.51	2.02	2.38	2.27
Yields, as % of total carbon burned to:					
CH_3OH	29.6	45.0	74.2	41.1	52.3
CH_2O	2.48	3.66	2.97	2.14	6.04
HCOOH	0.97	0.51	0 92	1.15	0.74
Total	33.05	49.17	78.09	44.39	59.08
Total inlet oxygen accounted for, %	78.0	70.0	78.5	67.5	77.5

The action of silver was not unexpected in view of its similarity to copper. It did not show visible signs of oxidation, as was always true of copper, but there was probably some adsorption of oxygen by the silver. The action of silver may be compared with that of copper by inspection of the results of Experiment 153, Table I. The only significant difference lies in formaldehyde production, silver producing about twice as much as copper. A greater activity on the part of silver, or the greater free space associated with the silver, would account for this greater degree of oxidation.

The steel catalyst was definitely poor in giving low yields and making control very difficult. This was expected in view of previous results (2) and also from the composition of the steel. While copper always showed evidence

of reaction with oxygen, the steel catalyst was unchanged before and after reaction. It showed no evidence of oxidation and reduction in that the surface was as smooth and bright after reaction as before. The steel was not inert, however, otherwise results similar to those found with glass would have been obtained. Evidently, the steel promoted complete oxidation.

Discussion

Inspection of the tables shows, on the basis of the carbon balance, an invariable loss of oxygen that ranges from 50 to about 10%. There is no relation evident between the oxygen loss and the conditions of the experiments. Further, in previous work (4), surplus oxygen was frequently found when natural gas was a reactant. Finally, in experiments at low temperatures where little reaction occurred, the oxygen balance was good. A search was made for an explanation of the oxygen balances. Obviously the catalyst might retain oxygen, and one reason for the use of glass was this possibility. However, the oxygen loss was as great with glass as with copper. Glass would not retain oxygen, and the copper walls of the reactor would not be expected to have more than a part of the capacity of the copper catalyst to retain oxygen. Similar remarks apply to the steel catalyst. The composition of the average gas samples was confirmed by analysis of instantaneous samples taken throughout an experiment. Further, the residual gas in the reactor after an experiment was withdrawn when the reactor was cool, and analyzed. The analysis agreed with that of the regular sample. The formation of gaseous oxygen compounds not detected in the methods of analysis used was highly improbable, but was examined. The off-gas was passed through a quartz tube maintained at 1100° C., a temperature high enough to destroy any compounds present with the production of carbon oxides and water. The oxygen content of the cracked off-gas was found to be the same as that of the off-gas itself. Confirmation of the methods of analysis of liquid condensates and off-gases by ultimate analysis has been mentioned. No solids or liquids were deposited in the reaction system. Impossible as it seemed, all the oxygen entering the system did not appear in the products. The only conclusion possible is that oxygen may be adsorbed, and possibly desorbed, in large amounts by the reactor, a conclusion that is questionable because of the large amounts of oxygen involved, and one that has still to be proved. Wiezevitch and Frolich (6) accounted for only 70% of the oxygen in experiments with natural gas and methane; with propane the recovery was only 40%. They offer no explanation.

Another observation with regard to oxygen should be pointed out. In nearly all experiments oxygen was found in the off-gases. This survival of oxygen was not expected, but was, nevertheless, real. Extreme care was taken in the sampling of the off-gases, and different methods were used, all with the same result—that oxygen survived. The only experiments where oxygen was absent in the off-gas consistently were those in which the empty reactor and steel as catalyst were used. This is suggestive in view of the lack

of control during such experiments, and suggests surface reactions under control as beneficial, and uncontrolled gas phase reactions going to completion as detrimental.

In view of the results presented in this and preceding papers (2, 4), a discussion at this time of the mechanism may be profitable. The general features of the results may be explained reasonably well by a mechanism involving features of the "hydroxylation" theory advanced by Bone (1) and a chain reaction theory advanced by Norrish (5). Obvious confirmation of the truth of Bone's theory lies in the production of large amounts of methyl alcohol together with formaldehyde and formic acid in small amounts. The dependence of yield on oxygen concentration and the necessity for high pressures are details explicable on the theory. Finally, tests for peroxides were always negative.

Bone's theory does not offer a satisfactory explanation, however, for many observations regarding the minor products of the reaction and the kinetics of the reaction. It is believed that Norrish's theory clears up many of these points, and the following theory, combining aspects of both, is presented.

The primary reactions suggested are two, a surface reaction between methane and oxygen and a homogeneous gas phase reaction between methane and oxygen. Both reactions require activated oxygen; in the first, the oxygen may be absorbed on the catalyst surface or combined with the catalyst, for example, as cuprous oxide, and in the second, the oxygen may be activated or in the atomic form. The source of the atomic or activated gaseous oxygen will be discussed later. The surface reaction may be written as:—

$$CH_4 + O_a \longrightarrow CH_3OH \qquad (1)$$

or

$$CH_4 + Cu_2O \longrightarrow CH_3OH + 2Cu.$$

The methanol may survive or proceed to formaldehyde or formic acid by Bone's mechanism through further oxidation. This reaction is required by Bone as the first stage in the oxidation of methane, and moreover it is admitted by Norrish as a reaction that occurs; according to Norrish's theory it plays the role of a chain breaker. The homogeneous reaction may be taken from Norrish as:—

$$CH_4 + O^+ \longrightarrow CH_2\!: + H_2O \qquad (2)$$

$$CH_2\!: + O_2 \longrightarrow CH_2O + O^+ \qquad (3)$$

a chain reaction that is broken by (1) above. The occurrence of the following reactions may be postulated also:—

$$n\,CH_2\!: \longrightarrow (CH_2)_n \qquad (4)$$

$$CH_2O \longrightarrow CO + H_2 \qquad (5)$$

or

$$CH_2O + \tfrac{1}{2}O_2 \longrightarrow CO + H_2O \qquad (6)$$

all of which are known to occur in other work.

Low oxygen concentrations favor methanol production, and one may conclude this from Reaction (1). This is only to be expected since with a limited supply, and a good catalyst, most of the oxygen in the reactive form will be on the catalyst. The methanol formed will survive in large part; to undergo further oxidation it would have to compete for oxygen with the much larger quantity of methane present. However, at high oxygen concentrations a considerable amount of activated oxygen may be expected in the gas phase. Methanol might be expected to oxidize further, the whole Bone series of reactions moving further toward carbon monoxide, carbon dioxide, and water.

A further and probably more important effect of high oxygen concentrations will be the promotion of the reactions in Norrish's theory, Reactions (2) and (3). These are homogeneous reactions and should be promoted by increased oxygen concentration in the gas phase, whereas Reaction (1) is heterogeneous and relatively independent of oxygen concentration once the catalyst surface is covered. Hence one might expect an increased production of aldehydes and higher hydrocarbons, Reaction (4), at high oxygen concentrations. However, aldehydes are very reactive compared to alcohols and hydrocarbons, and little would survive. Rather, an increased production of carbon monoxide, carbon dioxide, and water would result. In the methane experiments, the reduction in methanol yield, the production of carbon monoxide, and the increased traces of higher hydrocarbons at high oxygen concentrations is explicable on this basis. At low oxygen concentrations methanol is the primary product, and the amount of aldehyde formed is so small as to give no carbon monoxide. Reactions (3) and (4) are nearly, if not entirely, suppressed under these conditions. The occurrence of explosions at the highest oxygen concentration used is readily explained by Norrish's theory through the formation of aldehydes in large amounts. The reactive nature of the aldehyde, compared with methanol and methane, would account for the explosions.

To summarize,— it is postulated that two primary reactions occur, (1) and (2) above, the first being heterogeneous and desirable, and leading to the Bone mechanism of oxidation, the second being a homogeneous chain reaction yielding formaldehyde and gases but no methanol, and so undesirable. The relative proportion of each in the whole reaction depends mainly upon oxygen concentration, the proportion of the second increasing with increasing oxygen concentration.

Increasing the pressure of the reactants would affect the two reactions. With increasing pressure, Reaction (1) should be promoted through increased velocity and shift in equilibrium. Moreover, further reactions in the Bone series would be suppressed. However, the pressure of methane only would be effective, the effect of increased oxygen pressure being small, on the assumption that the catalyst is practically saturated with oxygen at all concentrations. Reactions (2) and (3) will be increased in velocity by increase in pressure or concentration of both methane and oxygen, with oxygen probably the more important reagent. These are detrimental reactions. The observed

result at low oxygen concentrations that there is a maximum in the pressure-yield relation follows from the above theory. As the pressure is raised at constant oxygen concentration, Reaction (1), the predominating reaction, and, at the same time, Reactions (2) and (3), are promoted. It is conceivable that the velocities of Reactions (2) and (3) increase more rapidly with pressure than does that of Reaction (1), the velocity depending on two reactants in the former case as against one reactant in the latter. Ultimately, and presumably at pressures higher than 184 atm. for the experiments in question, Reactions (2) and (3) predominate, and the yield of methanol falls. As the oxygen concentration in the gas is increased, the effect of pressure should change, Reactions (2) and (3) being favored at the expense of Reaction (1), and ultimately a decrease in pressure should favor Reaction (1). This was found to be the case at concentrations of 8 to 9% oxygen where the minimum pressure of 141 atm. gave the highest yield of methanol.

The effect of temperature is more or less obvious. Once the ignition temperature is reached, the effect of increased temperature is to increase the velocity of all reactions, the secondary reactions in both mechanisms as well as the primary. At sufficiently high temperatures, depending on the oxygen concentration, the oxidation and decomposition of the primary products, methanol and formaldehyde, to carbon monoxide, carbon dioxide, and water will be so extensive as to result in a decrease in yield. This has been observed, the optimum temperature being nearly independent of pressure but dependent on oxygen concentration.

The effect of space velocity on the reactions is not so clear. One might say at first sight that increasing rate of flow should result in increased yields of the primary products, but such was not the case. The conclusion to be drawn is that within the range of space velocity used, the reactions were always complete, or there was no time for further reaction. Neither methanol nor formaldehyde is stable with respect to the decomposition products, carbon monoxide and hydrogen, especially formaldehyde under the conditions used. However, the methane equilibrium, as well as the methanol equilibrium, with carbon monoxide and hydrogen will be set up, and in the presence of an excess of methane the whole system will shift toward methanol, a conception that may explain the survival of methanol independently of the time of contact. None of the catalysts are good catalysts for the methanol synthesis at high pressures, although copper is an excellent promoter of good catalysts. The alternative conception is that in the range of space velocities used, insufficient time was allowed for decomposition of methanol. Both conceptions may play a part. The low yield found in experiments with the empty autoclave is explicable on the basis of both space velocity and Norrish's chain reaction. The space velocity was much smaller in these experiments, and the time required for methanol decomposition may have been reached. The more likely explanation of the low yield, however, is the predominance of Reactions (2) and (3) through the large gas phase in the empty autoclave, with subsequent decomposition of the aldehyde formed.

While the action of catalysts has been discussed in part, some further remarks regarding the effect of glass and alloy steel may be of value in the light of the above-described mechanism. The inaction of alloy steel may be attributed to its failure to absorb or combine with oxygen to any extent. This alloy, of the stainless type, is characterized by its resistance to oxidation. Consequently only the copper walls of the reactor would promote Reaction (1), Reactions (2) and (3) taking place in the gas spaces between the steel chips. There would be a consequent fall in yield, as was observed.

The reason for the efficiency of glass as a catalyst is not clear. One can suggest that it is a good catalyst for Reaction (1) either through the adsorption of oxygen or methane, which is unlikely, or through some power of activation of the reactants. It is interesting to note that in the work of Bone and collaborators on the oxidation of methane at atmospheric pressures, surfaces such as porcelain, silica, or glass were the most effective in promoting aldehyde formation. The assumption made by Bone was, of course, that methanol was the primary product. As an alternative, it may be suggested that the glass was not a catalyst at all but served the purpose of a deactivator of oxygen, and broke the chains efficiently in Norrish's reaction. Consequently, the predominating reaction would be the formation of methanol on the copper walls of the reactor.

The efficiency of silver may be attributed to the same property effective with copper, namely, its ability to adsorb oxygen and its ease of oxidation and reduction. The greater solubility of oxygen in silver, with the possibility of a higher active concentration in the surface, may account for the increased formaldehyde production. Methanol may be oxidized to formaldehyde, or active oxygen may be liberated from the silver; this would promote Reactions (2) and (3).

In regard to experiments with natural gas (4), the behavior of ethane is of interest. Sometimes all or nearly all the ethane disappeared, the amount of methanol produced comparing with the amount of ethane oxidized and frequently being greater. More interesting however are those experiments in which the amount of ethane in the off-gas was nearly the same as that in the in-gas. Connected with the ethane is the reduction in temperature of the reaction when natural gas was used. Ethane appeared to promote oxidation of the methane at temperatures lower than normal. The oxidation of ethane may be considered to proceed according to the following mechanism:—

$$\begin{array}{ccc} & & CH_3 - CH_3 + \tfrac{1}{2}O_2 \longrightarrow CH_3 \cdot CH_2 \cdot OH \\ & & + \\ & & O_2 \\ & & \downarrow \\ & & CH_3 \cdot CHO + H_2O \\ +\tfrac{1}{2}O_2 & \swarrow & \searrow \\ CH_3OH + CO & & CH_4 + CO \end{array}$$

Between ethane and acetaldehyde, an intermediate stage analogous to Reaction (2) in Norrish's theory may intervene. The condensates from the natural gas experiments showed traces of ethyl alcohol by the iodoform test; this confirmed at least one reaction. No ethyl alcohol could be detected in the condensates from the methane experiments. The formation of acetaldehyde with its subsequent oxidation to methyl alcohol will explain the observed results that frequently the ethane burned could account for most of the methanol formed. The oxidation of the methane at low temperatures may be accounted for by assuming the decomposition of acetaldehyde to produce activated molecules, the methane being able to react directly with the oxygen and the carbon monoxide to activate other methane molecules. Alternately, as in Norrish's theory, we may assume the formation of free radicles from the ethane which are able to activate either methane or oxygen. Those experiments in which the ethane apparently survived are explicable on the basis of free methylene groups formed according to Reaction (2) of Norrish's mechanism. They will polymerize as in Reaction (4), and may be hydrogenated with the formation of ethane. More probable is the formation of cyclopropane, a fairly stable hydrocarbon easily mistaken for ethane in the methods of gas analysis used. While all gas analysis combustions were performed in duplicate and checked, the small amounts of higher hydrocarbons above methane found could easily have been ethane or cycloparaffins. The method of calculation, based on a small difference in large quantities, was such that ethane would not be distinguished from cyclopropane in the gas. The presence of higher cycloparaffins would interfere with the carbon monoxide and hydrogen determinations, and may account for the difficulties of analysis found with some of the natural gas experiments.

Finally, the bearing of the results on the utilization of natural gas may be discussed. The yields of methanol obtained, 75% as a maximum on the basis of carbon oxidized, are high, and can without doubt be raised. However, the conversion of total carbon in the system to methanol is very low, and probably not of commercial value even in a circulatory process. Further experiments in which oxygen in place of air is used are in progress, and they give results comparable to those found with air. Attempts to suppress the undesirable reactions occurring at high oxygen concentrations and the use of a circulatory process are in preliminary stages. At least 5% of the ingoing carbon, and preferably more, converted to methanol with high efficiency per pass is necessary to give the process practical possibilities.

References

1. BONE, W. A. Proc. Roy. Soc. (London), 134A : 243-274. 1932.
2. BOOMER, E. H. and BROUGHTON, J. W. Can. J. Research, B, 15: 375-382. 1937.
3. BOOMER, E. H., JOHNSON, C. A. and THOMAS, V. Can. J. Research, B, 15: 360-362. 1937.
4. BOOMER, E. H. and THOMAS, V. Can. J. Research, B, 15: 401-413. 1937.
5. NORRISH, R. G. W. Proc. Roy. Soc. (London), 150A: 36-57. 1935.
6. WIEZEVITCH, P. J. and FROLICH, P. K. Ind. Eng. Chem. 26: 267-276. 1934.

DERIVATIVES OF SUBSTITUTED SUCCINIC ACIDS

III. THE ACTION OF ALKALINE SODIUM HYPOBROMITE ON PHENYLSUCCINAMIDE AND $\alpha\alpha'$-DIMETHYLSUCCINAMIDE[1]

By John A. McRae[2], Arthur W. Weston[3], and Charles F. Hubbs[4]

Abstract

Previous work on the action of alkaline sodium hypobromite on $\alpha\alpha'$-diarylsuccinamides has been extended to include phenylsuccinamide and $\alpha\alpha'$-dimethylsuccinamide, typical respectively of monoaryl- and $\alpha\alpha'$-dialkyl-succinamides. Phenylsuccinamide and sodium hypobromite give β-ureidophenyl-propionic acid and phenyldihydrouracil, but no phenylacetic acid. Likewise dimethylsuccinamide gives dimethyldihydrouracil and no isobutyric acid. Hence the rearrangement observed with diarylsuccinamides does not occur with these two amides.

Introduction

Amides of the succinic acid type have been found to act in two different ways toward alkaline sodium hypobromite in the Hofmann reaction. Thus while succinamide and methylsuccinamide (9) give dihydrouracil and methyldihydrouracil respectively, diphenylsuccinamide (6), and *p*-methyl-, *p*-chloro-, and *p*-bromo-diphenylsuccinamide (5) give *p*-diphenylacetic acid and *p*-methyl, *p*-chloro- and *p*-bromo-diphenylacetic acid respectively. It has seemed desirable to study the behavior of other differently substituted succinamides to ascertain the effect that substituents have in modifying their behavior in the Hofmann reaction. In the present paper a report is made on the action of sodium hypobromite on *phenylsuccinamide* as typical of monoarylsuccinamides and on dimethylsuccinamide representing $\alpha\alpha'$-dialkylsuccinamides.

Both of these amides behave much like methylsuccinamide in the Hofmann reaction. However, instead of 6-phenyldihydrouracil we obtained, from phenylsuccinamide, β-ureidophenylpropionic acid, $C_6H_5 . CH(NH . CONH_2) . CH_2 . CO_2H$, which was identified by direct comparison with a sample of this substance made according to the modification of Fischer's method used by Evans and Johnson (3). It was identified further by converting it into phenyldihydrouracil, again using an authentic specimen for comparison. In one experiment on phenylsuccinamide in which conditions were varied slightly, the action of the hypobromite produced phenyldihydrouracil directly. Before isolation of the β-ureidophenylpropionic acid, steam was passed into the acidified solution for some time, and the distillate examined for phenylacetic acid. No trace of this acid was observed and consequently there was no indication that rearrangement had occurred. By the action of sodium hypobromite on phenylsuccinamide conceivably 5-phenyldihydrouracil and the corresponding acid, α-ureidomethyl-phenylacetic acid, $C_6H_5 . (NH_2 . CONH . CH_2) . CH . CO_2H$, might have been formed, but neither of these substances was isolated.

[1] *Manuscript received July 15, 1937.*
Contribution from the Chemical Laboratories, Queen's University, Kingston, Canada.
[2] *Professor of Chemistry, Queen's University.*
[3] *Leonard Fellow (1934-1935), Queen's University.*
[4] *Milton Hersey Fellow (1935-1936), Queen's University.*

Cis-$\alpha\alpha'$-dimethylsuccinamide under the same treatment gave *5,6-dimethylhydrouracil*, as shown by a direct comparison with a specimen of this substance made by the application of the general directions of Fischer and Roeder (4) to tiglic acid with which it was found to be identical. As in the previous instance, steam distillation following acidification of the reaction mixture gave no trace of isobutyric acid, which would have been formed had a rearrangement occurred similar to that observed with diarylsuccinamides.

Phenylsuccinamide was made by the action of ammonia either on methyl phenylsuccinate, a reaction that takes place very slowly, or on phenylsuccinimide, which is the method to be preferred. Although Morrell (7) found that succinyl chloride and ammonia gave extremely poor yields of succinamide, it was hoped that the action of ammonia on phenylsuccinyl chloride would prove a rapid method, but using a variety of conditions only very small yields of phenylsuccinamide were obtained. Unsuccessful efforts were made to convert the product formed by the addition of hydrogen cyanide to ethyl α-cyano-β-phenylacrylate, presumably $C_6H_5CH(CN) \cdot CH(CN)CO_2Et$, into phenylsuccinamide.

Authentic cis- and trans-dimethylsuccinamides were made first by Morrell (7) by the action of concentrated ammonia on cis- and trans-dimethyl dimethylsuccinates, but the reaction is very slow and the yields of the amides obtained are rather low. We found that by adding ammonia to dimethylsuccinimide, filtering off the amide formed, evaporating to dryness, and again adding ammonia, finally an almost quantitative yield of the cis-amide could be obtained. After some preliminary experiments with other methods, that of Morrell was followed in making dimethylsuccinic acid according to Zelinski's procedure (10).

Experimental

PHENYLSUCCINIC DIAMIDE $C_6H_5 \cdot CH(CONH_2) \cdot CH_2 \cdot CONH_2$

(a) From Dimethyl Phenylsuccinate

A mixture of dimethyl phenylsuccinate (10 gm.), dissolved in the minimum quantity of methyl alcohol (100 cc.), with 5 cc. of concentrated ammonia was allowed to stand for two weeks. The crystalline deposit which gradually formed was collected, and the remaining solution evaporated to dryness. The crystalline deposit and the latter residue were washed with acetone to remove unchanged ester. The amide thus obtained was recrystallized repeatedly from alcohol; m.p.* 211° C. Calcd. for $C_{10}H_{12}O_2N_2$: C, 62.50; H, 6.25; N, 14.58%. Found: C, 62.31; H, 6.35; N, 14.61%. The residual alcoholic liquors gave a small amount of material soluble in water. On acidification this gave a substance having on recrystallization the properties described by Anschütz (1) for the β-amide of phenyl-succinic acid, $C_6H_5 \cdot CH(CO_2H) \cdot CH_2 \cdot CONH_2$; m.p. 145° C.

**Melting points are uncorrected.*

(b) From Phenylsuccinimide

Phenylsuccinimide was made either by distilling in a retort phenylsuccinic acid in a current of dry ammonia, or by heating ammonium phenylsuccinate under reduced pressure. The yield was about 70% by either method. Phenylsuccinimide (28 gm.) was dissolved in 50 cc. of concentrated ammonia. On standing for two days, phenylsuccinamide separated as a crystalline mass, and after filtration and washing with water to remove ammonium phenylsuccinate it was recrystallized from alcohol. The original ammoniacal mother liquor on evaporation gave a further quantity of the amide. Total yield: 18 gm. or 60% of the calculated yield.

(c) From Phenylsuccinyl Chloride

The chloride was made from phenylsuccinic acid and phosphorus pentachloride according to the directions of Anschütz (1). On adding slowly this chloride, with efficient stirring, to concentrated ammonia at $-10°$ C., a precipitate was obtained from which a small amount, namely 4% of that calculated, of phenyl succinamide was isolated. The principal products isolated were phenylsuccinic acid and the β-amide of phenylsuccinic acid; m.p. 145° C. Grinding the acid chloride with ammonium carbonate or adding it to dry ammonia dissolved in dry ether gave no better results.

Action of Sodium Hypobromite on Phenylsuccinamide

Phenylsuccinamide (6.9 gm.) made into a thin paste with 100 cc. of water was added slowly with efficient stirring to a sodium hypobromite solution made from 20 gm. of caustic soda in 100 cc. of water and 16 gm. of bromine. The temperature was maintained at $-5°$ C. during the addition of the amide, and it was then allowed to rise to room temperature; 12 gm. of caustic soda was then added and the mixture heated to 75° to 80° C. on the water bath for three hours. Contrary to the behavior of diphyenylsuccinamide, no ammonia was evolved. The alkaline solution was extracted with ether, but after removal of the ether from the extract nothing remained. Acidification gave a mass of crystals (7.2 gm.) which proved to be β-ureido-β-phenylpropionic acid. Recrystallized repeatedly from either alcohol or water, the substance melted at 191° C., the value given by Posner (8) and by Dakin (2) and confirmed by Evans and Johnson (3). A mixed melting point determination with β-ureido-β-phenylpropionic acid made from urea and cinnamic acid caused no depression of the melting point. Calcd. for $C_{10}H_{12}N_2O_3$: N, 13.46%. Found: N, 13.76%. Equivalent calcd: 208. Found: 208. The product was identified by converting it into 6-phenylhydrouracil, the melting point after several recrystallizations, 217° C., agreeing with the figure given by Posner and by Dakin. Likewise, it did not depress the melting point of authentic 6-phenyldihydrouracil. In one experiment with phenylsuccinamide 6-phenyldihydrouracil was isolated as the principal product of the reaction.

Meso-α,α'-dimethylsuccinamide

Dimethylsuccinic acid was made according to the directions of Zelinski (10). It was converted into its ammonium salt, and this on heating at 200° to 220° C. in an atmosphere of dry ammonia gas gave the dimethylsuccinimide in 80% yield, as described by Zelinski and Krapivin (11).

Dimethylsuccinimide was converted into the amide by dissolving it in the minimum amount of concentrated ammonia and allowing it to stand for 24 hr. A quantity of amide had separated. This was filtered and recrystallized. The filtrate was evaporated to dryness and dissolved in concentrated ammonia. This on standing gave a further quantity of amide. The process was repeated several times. Ultimately an almost quantitative yield of the amide was obtained. Better results were obtained in this manner than by allowing the filtrate to stand. The amide on recrystallization melted at 244° C. with decomposition. Morrell describes the cis-form as melting at 244° C. The "cis-form" is obviously the meso-form. The same product was obtained in small yield from dimethyl dimethylsuccinate.

Action of Alkaline Sodium Hypobromite on meso-Dimethylsuccinamide

Dimethylsuccinamide (4.3 gm.) was treated with alkaline sodium hypobromite under conditions strictly parallel to those previously described for phenylsuccinamide. After the reaction mixture had been heated on the water bath, the solution was acidified and steam distilled. No isobutyric acid could be detected in the distillate. The residual solution was evaporated to dryness and the residue extracted thoroughly with hot alcohol. After evaporation of the alcohol a crystalline residue was obtained which was repeatedly recrystallized from alcohol; m.p. 204° to 205° C. It separated in shining plates. The substance did not depress the melting point of 5,6-dimethyldihydrouracil synthesized as described below. Calcd. for $C_6H_{10}O_2N_2$: C, 50.6; H, 7.04; N, 19.7%. Found C, 50.4; H, 7.25; N, 19.8%.

5,6-Dimethyldihydrouracil

The procedure of Fischer and Roeder (4) was applied to tiglic acid. Tiglic acid (10 gm.) was heated with 6.3 gm. of urea to 210° to 220° C. until foaming ceased. The brown melt was recrystallized from hot alcohol; this gave characteristic shiny mica-like crystals, m.p. 204° to 205° C. The yield, based on the tiglic acid used, was 32%. Calcd. for $C_6H_{10}O_2N_2$: N, 19.7%. Found: N, 19.9%.

Acknowledgment

The authors express their thanks to Mr. J. A. Martin who prepared the dimethyldihydrouracil from tiglic acid.

References

1. ANSCHÜTZ, R. Ann. 354 : 117-151. 1907.
2. DAKIN, H. D. J. Biol. Chem. 8 : 35-39. 1910.
3. EVANS, J. and JOHNSON, T. B. J. Am. Chem. Soc. 52 : 4993-5005. 1930.
4. FISCHER, E. and ROEDER, G. Ber. 34 : 3751-3763. 1901.
5. McRAE, J. A., CONN, W. R. and PLATT, K. J. Can. J. Research, B, 15 : 46-51. 1937.
6. McRAE, J. A. and TOWNSHEND, A. S. Can. J. Research, 11 : 628-636. 1934.
7. MORRELL, G. F. J. Chem. Soc. 105 : 2698-2707. 1914.
8. POSNER, T. Ber. 38 : 2316-2325. 1905.
9. WEIDEL, H. and ROITHNER, E. Monatsh. 17 : 172-190. 1896.
10. ZELINSKI, N. Ber. 21 : 3160-3172. 1888.
11. ZELINSKI, N. and KRAPIVIN, S. Ber. 22 : 646-654. 1889.

THE CATALYTIC DEHYDRATION OF ETHYL ALCOHOL BY ALUMINA. II.[1]

By W. A. Alexander[2], W. R. Horn[3], and L. A. Munro[4]

Abstract

The decomposition of ethyl alcohol by two different samples of commercial alumina at 318° and 450° C. has been studied. The effect of time or previous use of the catalyst on the course of the reaction has been examined at 300° and 318° C. It has been found that the course of the reaction changes with change in water content of the catalysts. For the particular alumina used, there is one optimum water content for the production of ether and another for ethylene. For catalysts initially high in water there is a change in the sense of the reaction with use. Ignited catalysts of zero water content are not inactive, but become less effective for dehydration; this favors the production of ether.

The effect of the water content of alumina gel on its efficiency as a catalyst for the production of ether from ethyl alcohol has been reported previously (14). It was found in the above-mentioned investigation that at 250° C. ether only was obtained from initial dehydration runs on catalysts of the same origin but differing in water content. There was, however, a distinct optimum water content of the catalyst for this reaction.

Further work was undertaken to ascertain whether, at a higher temperature, the efficiency of the dehydration to ethylene was also dependent on the water content of the catalyst. It was also determined to ascertain whether, at some intermediate temperature at which both ethylene and ether are produced, the course of the reaction could be changed in favor of one or other of the products of reaction by change in water content of the catalyst.

Apparatus

The apparatus employed in this investigation was essentially similar to that used previously, except that an intermediate condensing worm cooled in ice was inserted between the furnace and the receiver that was cooled with solid carbon dioxide. This prevented the occasional clogging of the system by the freezing of the water produced by the reaction.

Commercial absolute alcohol was used. This had a refractive index of 1.3633 at 15° C. as compared with 1.3637 at 15° C. as given by Sanfourche and Boutin (18) for pure alcohol. The alumina used initially was the same as that employed in the previous work. The product was first dried at 110° C. for eight hours, and then broken up so as to pass through a 6 to 10 mesh screen.

[1] *Manuscript received June 28, 1937.*
Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada.

[2] *Arts Research Fellow, 1935–1936, Department of Chemistry, Queen's University.*

[3] *At the time, graduate student, Department of Chemistry, Queen's University; at present, member of technical staff, Eldorado Radium Refinery, Port Hope, Ontario.*

[4] *Associate Professor of Chemistry, Queen's University.*

Experimental

Activation of Catalyst

The gels were activated by heating a weighed amount of catalyst in an electric furnace for two hours, for the runs at 450° C., and for one hour for the lower temperature runs. The temperature was measured by means of a thermocouple and was maintained constant (±2°) by hand regulation of the rheostats. A constant slow stream of nitrogen (1 cc. per sec.) was passed through the catalyst tube during activation and cooling, although it was found that doubling the rate of flow of the nitrogen did not appreciably affect the residual water content.

The literature contains numerous references to the temperature of activation, the assumption being that *this* is the factor which determines the activity of a catalyst. Identical catalysts are not always obtained, although the activation is carried out at the same temperature for the same time and with the same flow of nitrogen. The resulting catalysts may differ in water content and activity. In the writers' experience, the resulting water content is a better criterion of activity than the temperature of activation.

If the total water content of the gel (determined by "blasting" to zero water content over a Méker burner) and the loss in weight on activation are known, the residual water content may be calculated. In these experiments this residual water is expressed as percentage of the weight of the activated catalyst. The activation temperatures chosen were always higher than the reaction temperatures used. This limits the range of water content of the catalysts obtainable for the higher reaction temperature, since all but 5.5% of the water is removed by activation for two and a half hours at 450° C. (14).

Analyses

Ether in the distillate was determined by Kunke's method (10).

The volume of gas produced was measured by displacement of saturated brine solution. Analysis showed that it was almost pure ethylene, with 1 to 2% of hydrogen and a trace of saturated hydrocarbons.

Semi-quantitative tests for the aldehyde content of the distillate were made (2). Appreciable quantities were found in all cases. The values for the high temperature runs range from 0.4 to 1.0%, and for the low temperature runs, from 0.1 to 0.4%. Ipatieff (9, p. 69) states that aldehydes are produced as a result of the presence of oxygen in the system.

High Temperature Runs—450° C.

Alcohol (20 cc.) was passed over different catalysts having residual water contents varying from 0 to 5.5%. The duration of the runs was 75 min. The theoretical yield of 8.1 litres of gas was obtained with all catalysts. Second runs with the same catalysts gave identical results. It is obvious that at this temperature there is no optimum water content as there is in the low temperature dehydration. Ipatieff (9, p. 69), in his book which appeared since this work was completed, reports that 420° to 450° C. is the optimum temperature for the production of ethylene from ethyl alcohol when alumina is used, but that the reaction "begins at 360°".

Runs at Intermediate Temperature—318° C.

A series of catalysts ranging in water content from 0 to 14.7% were used for the runs at 318° C. Twenty-five cubic centimetres of alcohol were passed over the catalyst in 90 min. Two runs were made with each catalyst. The detailed results of these runs are given in Table I. The runs at 450° C. were carried out in tubes Nos. 1–4. Column six represents the ratio of the number of moles of alcohol decomposing to ethylene, to the number of moles of alcohol decomposing to ether. This is an index of the course of the reaction and is plotted in Fig. 1.

TABLE I

RUNS AT 318° C.—B.D.H. ALUMINA

Tube, and Run No.	Water in gel, %	Activation temp., °C.	*A* Per cent ether in distillate	*B* Ethylene, litres	*B/A*, moles	Moles alcohol decomposed / Moles alcohol supplied (S) × 10^2		
						A/S	*B/S*	$\frac{A+B}{S}$
5 *A*	14.7	318	4.6	0	0	5.7	0	5.7
B			7.8	0	0	9.7	0	9.7
6 *A*	10.0	350	6.9	0	0	8.6	0	8.6
B			2.1	0	0	2.6	0	2.6
7 *A*	7.9	380	1.6	0	0	2.0	0	2.0
B			1.4	0.20	1.2	1.7	2.0	3.7
8 *A*	4.2	410	6.9	0.60	0.7	8.6	5.9	14.5
B			1.4	0.58	3.5	1.7	5.8	7.5
9 *A*	5.4	400	13.5	1.05	0.7	16.8	10.4	27.2
B			13.6	1.10	0.7	17.0	10.8	27.8
10 *A*	3.2	500	1.3	1.58	11.4	1.6	16.0	17.6
B			2.4	1.59	6.2	3.0	16.0	19.0
11 *A*	1.2	605	2.9	2.88	10.9	3.6	28.0	31.6
B			2.4	2.15	8.2	3.0	21.0	24.0
12 *A*	0		1.8	1.19	5.6	2.2	12.0	14.2
B			1.9	1.30	6.0	2.4	13.0	15.4

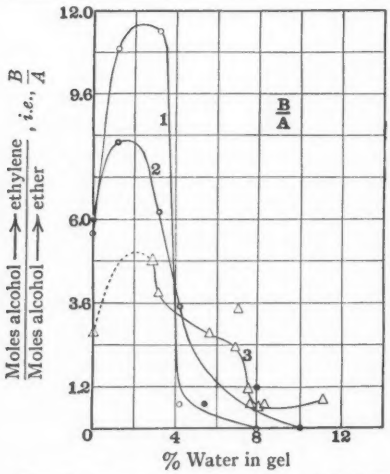

FIG. 1. *Course of reaction. Curve 1, B.D.H. alumina, A runs, 318° C. Curve 2, B.D.H. alumina, B runs, 318° C. Curve 3, St. L. I. alumina, A runs, 300° C.*

It will be observed that the course of the reaction changes with change in the water content of the activated catalyst, and further, that the ratio passes through a maximum for a water content of approximately 2% residual water. When the water content of the gel was greater, no

ethylene was produced, but the catalyst was still active for the production of ether (Fig. 2).

Columns 7, 8, and 9 in Table I show the molar efficiencies of the decomposition of the alcohol to ether, ethylene, and total dehydration, respectively. These are shown graphically in Figs. 2 and 3.

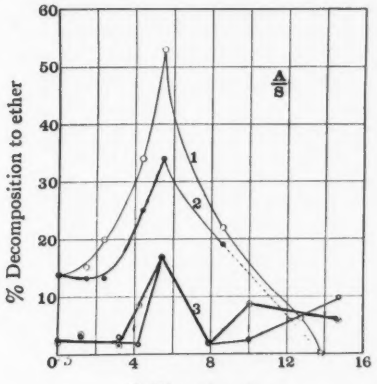

FIG. 2. *Efficiency of decomposition to ether. Curve 1, B.D.H. alumina, A runs, 250° C. Curve 2, B.D.H. alumina, B runs, 250° C. Curve 3, B.D.H. alumina, intermediate, A and B, 318° C.*

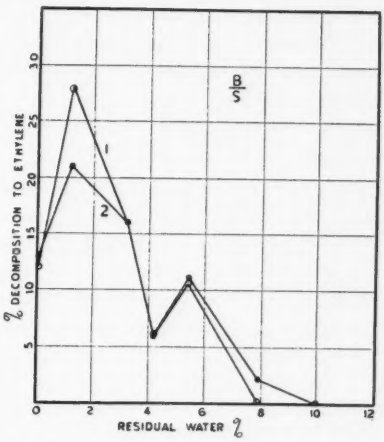

FIG. 3. *Change in efficiency of catalyst in the production of ethylene.*

In Curves 1 and 2, Fig. 2, the results obtained previously at 250° C. (14), when no ethylene was produced, are replotted as efficiencies for comparison with the present work. It will be noted that the optimum yield of ether occurs at the same gel water content.

Fig. 3 shows the change in efficiency of the catalyst in the production of ethylene. Here optimum activity is reached at 2% gel water.

The variation of total catalytic activity with residual water is plotted in Fig. 4. This shows two maxima in the total reaction corresponding to those for ether and ethylene as noted above.

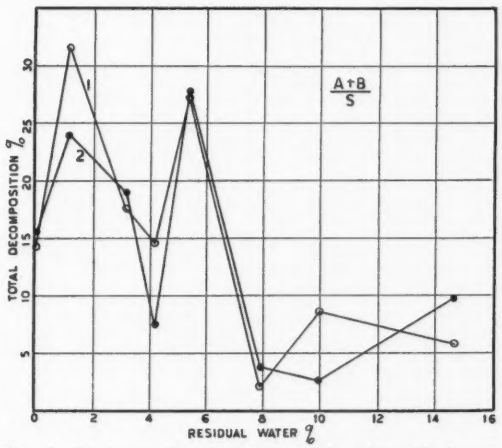

FIG. 4. *Variation of total catalytic activity with residual water.*

Variation in Efficiency with Use

It was noticed that an increased amount of ethylene was obtained from the second runs in Tubes 7 and 9 (Table I), and also an increased quantity of ether was obtained in several cases. This seemed to merit further investigation.

It would be expected that any change in catalytic activity with use would be most pronounced with gels of large water content. Activation can be considered, in part, as accelerated aging, and these gels have been activated (aged) to a lesser extent. There might also be some change in water content induced by use, even though the reaction temperature is lower than the activation temperature. Such a change would affect the course of the reaction as shown above.

Accordingly, two series of runs were made with Tubes 5 and 6 (Table I). The catalysts contained 14.7 and 10.0% residual water respectively. The results are given in Table II, where the headings of the columns have the same meaning as in Table I. The results are plotted in Figs. 5 and 6. It is evident from the figures that the indications of increased activity and change in the course of the reaction were realized in both cases.

TABLE II

EFFECT OF TIME OR USE—318° AND 300° C.

Tube, and water, %	Run	*A* ether in distillate, %	*B* Ethylene, cc.	*B*/*A*, moles	$\frac{\text{Moles alcohol decomposed}}{\text{Moles alcohol supplied } (S)} \times 10^2$		
					A/*S*	*B*/*S*	$\frac{A+B}{S}$
5	*A*	4.6	0	0	5.7	0	5.7
14.7	*B*	7.8	0	0	9.7	0	9.7
	C	1.9	290	1.2	2.4	2.8	5.2
	D	2.4	570	1.9	3.0	5.6	8.6
	E	3.3	580	1.4	4.1	5.7	9.8
	F	1.2	340	2.3	1.5	3.3	4.8
	G	1.1	380	2.8	1.4	3.7	5.1
	*H**	0.5	80	1.6	0.7	1.0	1.7
	*I**	0.9	70	0.8	1.1	0.8	1.9
	*J**	0.5	70	1.3	0.6	0.8	1.4
6	*A*	6.9	0	0	8.6	0	8.6
10.0	*B*	2.1	0	0	2.6	0	2.6
	*C**	1.8	110	0.5	2.2	1.1	3.3
	*D**	0.7	120	1.4	0.9	1.2	2.1
	*E**	0.6	100	1.3	0.7	1.0	1.7
	*F**	0.9	100	0.9	1.1	1.0	2.1
	*G**	0.4	80	1.7	0.5	0.8	1.3
	*H**	0.3	140	4.9	0.4	1.8	2.2
	*I**	0.16	120	6.4	0.2	1.3	1.5
	*J**	0.4	90	1.9	0.5	1.0	1.5
	*K**	0.7	90	1.1	0.9	0.9	1.8
	*L**	0.8	90	0.9	1.0	0.9	1.9

* *Carried out at 300° C.*

The curve A/S for Tube 5 (Fig. 5, curve 1) suggests a periodic reaction. Periodic reactions have been observed in a number of catalytic decompositions, the explanation for which has yet to be found (12, p. 60). The evolution of ethylene by Catalyst 5 shows a decided maximum (Fig. 5, Curve 2). The

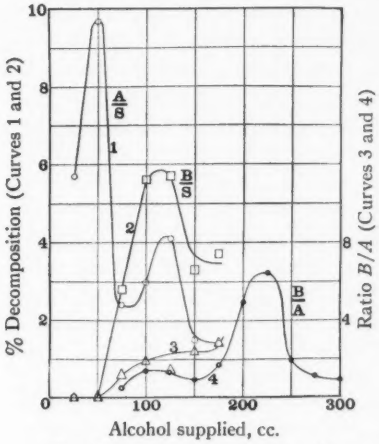

FIG. 5. *Change in sense of catalyst with use. Curves 1, 2 and 3, Tube 5, 318° C. Curve 4, Tube 6, 300° C.*

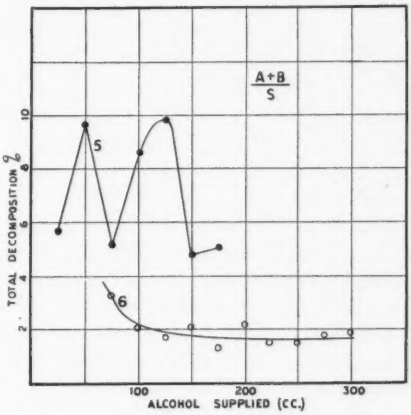

FIG. 6. *Total efficiencies of decomposition for Tubes 5 and 6.*

course of the reaction, given by the ratio B/A, is plotted in Fig. 5, Curves 3 and 4. The curve for Tube 6 shows a decided change in sense of the catalyst, with a subsequent return to the first ratios. The total efficiencies of decomposition for Tubes 5 and 6 are plotted in Fig. 6. Curve 5 shows evidence of a periodicity in the total reaction, while Curve 6 shows no such evidence. It is worth noting, however, that the proportion of molecules decomposing to ethylene has meanwhile passed through a maximum.

In a recent paper by Bliss and Dodge (4) the change in efficiency with use for the production of ethylene at 360° C. is shown for a number of alumina and mixed catalysts. In most cases a decrease in activity was observed, but with several catalysts an increase was found. No data are given regarding the initial water content of the catalysts.

A number of runs were made at 300° C. in which a sample of "Activated Alumina" supplied by the Aluminum Ore Co., E. St. Louis, Illinois, was used. Unfortunately this alumina was found to give so small a total decomposition (1 to 2.5%) that the accuracy of the observations was considerably decreased. The slight variation in total efficiency with changing residual water content is of doubtful significance. However, the ratio of the number of moles of alcohol decomposing to ethylene, to the number of moles of alcohol decomposing to ether, was evaluated, and is plotted in Fig. 1. The shape of the curve approximates that obtained with the B.D.H. sample of alumina, although the quantities involved are much smaller.

The inactivity of this catalyst is probably due to the presence of a small residue of alkali in the alumina (5). A positive test with phenolphthalein was obtained when the alumina was boiled with water. Bliss and Dodge (4) also record the very low efficiency of a commercial "active alumina" in the decomposition of alcohol.

Discussion

It is common experience that when the flow method is used it is difficult to obtain concordant absolute values for the products of reaction for duplicate runs. Adkins and Lazier (1), who have drawn attention to this fact, point out that the ratio of the reactions was unchanged, that is, that differences in total activity did not affect the ratio of quantities of products. The plot of this ratio, given in Fig. 1 for successive runs, shows definite agreement in change in the course of the reaction with gel water content and with time.

Sabatier and Reid (17) state that preparations of anhydrous alumina that have been heated to redness for a long time have almost no activity in the decomposition of alcohol, even at 420° C. The catalyst with zero water content (Table I), obtained by blasting alumina over a Méker burner for 48 hr., showed a high total activity (Figs. 3 and 4). While the total activity decreases as zero water content is approached, it does not fall to zero as would be expected from certain theories of catalysis (7).

The production of ethylene requires the elimination of one molecule of water from each molecule of alcohol, whereas in the formation of ether, one molecule is removed from two molecules of the alcohol. The ratio of ethylene to ether, *i.e.*, the greater to the less dehydration, decreases from 2 to 0% water content (Fig. 1).

It seems to be the accepted idea that ignition produces sintering with a decrease in pore size (3). It might be, however, that a fusion of finer pores would first occur. This would decrease the available surface, but would actually result in a relatively greater number of large pores. It is known that aging and heating produce increased size of pores in silica gel (13, p. 171), and it is to be expected that alumina would undergo the same change. Bancroft and George (3) obtained a catalyst with large pores by heating the hydrated nitrate, and this preparation was the best dehydration catalyst.

Increase in the efficiency of dehydration with decreasing gel water content may be partly explained on the basis of the results of Bancroft and George. The persistent but decreased dehydration activity of the ignited (or blasted) samples may point to a decrease in the total number of these larger pores. It may be noted that the total activities of the B.D.H. alumina with zero water content were the same at 250° and 318° C. This may be fortuitous, or may point to the same final gel structure in both cases.

There may also be several reasons for the change in the specificity of the catalyst with time. First, it may be due to accelerated aging, in which case the effect would be greatest for gels of high water content. This has been found to be true (Fig. 5). Aging, as has been shown, will produce

larger pores, and this favors the production of ethylene. While the curves obtained with Tube 5 resemble those for the change in efficiency with decreasing water content, the curves obtained with Tube 6 show an almost constant total activity; this precludes activation by loss of water as the cause of changing activity. Second, it may be that the proportion of the reactants and products of reactants on the surface changes with time owing to sorption. There is probably an optimum distribution of reactant molecules on the surface of the catalyst for the production of ether, and another for the production of ethylene. Munro and McCubbin (16) found that there is an optimum adsorption ratio of reactants for the reaction

$$CS_2 + 2H_2O \longrightarrow CO_2 + 2H_2S,$$

catalyzed by alumina. This adsorption ratio is probably an important factor in the change in catalytic activity with change in gel water content.

It has been shown that the amount of water unremoved by the activation of a given sample of alumina gel determines its adsorptive properties (15, p. 323) and catalytic activity, probably because the loss of gel water by heat treatment involves (1) increase in available surface, (2) change in porosity, and (3) in a measure, the extent of changes denoted by "aging", shown by several to involve also a change in X-ray patterns (22, 23).

Long, Frazer, and Ott (11) find that a relation exists between the arrangement of metal catalyst atoms in the crystal and the activity in promoting the reaction between hydrogen and benzene to form cyclohexane. These authors give several references to other papers indicating the dependence of catalytic activity and lattice dimensions. To these may be added papers by Eisenhut and Kaupp (6) and Storfer (20).

Wagner, Schwab, and Staeger (21), however, have shown that no change in crystal structure occurred with a promoted cupric oxide catalyst corresponding to its increase in activity. Smith and Hawk (19) investigated the crystal structure of oxide catalysts for the decomposition of methyl alcohol. They found no characteristic lines for their most active catalyst. Griffith and Hill (8) reached similar conclusions.

It has been shown that aluminas yield α-alumina on ignition. Preliminary X-ray studies on the writers' catalysts have not shown to what degree the crystal pattern of the gel fibrils is of importance.

Gels prepared by different methods being initially different in these several factors would not be expected to change in the same manner with loss of similar amounts of water. This aspect of the work is being investigated further.

Acknowledgments

The authors wish to express their indebtedness to Dr. W. H. Barnes of McGill University for his supervision of the X-ray studies, and to the Research Committee of Queen's University for a grant-in-aid.

References

1. ADKINS, H. and LAZIER, W. A. J. Am. Chem. Soc. 48 : 1671-1677. 1926.
2. ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Blakiston, Philadelphia, 4th ed. Vol. 1. 1909.
3. BANCROFT, W. D. and GEORGE, A. B. J. Phys. Chem. 35 : 2943-2949. 1931.
4. BLISS, R. H. and DODGE, B. F. Ind. Eng. Chem. 29 : 19-25. 1937.
5. CLARK, R. H., GRAHAM, W. E., and WINTER, A. G. J. Am. Chem. Soc. 47 : 2748-2754. 1925.
6. EISENHUT, O. and KAUPP, E. Z. Elektrochem. 36 : 392-403. 1930.
7. FRICKE, R. Kolloid-Z. 69 : 312-324. 1934.
8. GRIFFITH, R. H. and HILL, S. G. Proc. Roy. Soc. London, 148A: 194-206. 1935.
9. IPATIEFF, V. N. Catalytic reactions at high pressures and temperatures. MacMillan, New York. 1936.
10. KUNKE, W. F. J. Assoc. Official Agr. Chem. 16 : 348-361. 1933.
11. LONG, J. R., FRAZER, J. W., and OTT, E. J. Am. Chem. Soc. 56 : 1101-1106. 1934.
12. MAXTED, E. B. Catalysis and its industrial applications. Churchill, London. 1933.
13. MCBAIN, J. W. Sorption of gases and vapours by solids. Routledge, London. 1932.
14. MUNRO, L. A. and HORN, W. R. Can. J. Research, 12 : 707-710. 1935.
15. MUNRO, L. A. and JOHNSON, F. M. G. Can. J. Research, 10 : 321-331. 1934.
16. MUNRO, L. A. and MCCUBBIN, J. W. Proc. Roy. Soc. Can. III, 27 : 29-33. 1934.
17. SABATIER, P. and REID, E. E. Catalysis in organic chemistry. Van Nostrand, New York. 1922.
18. SANFOURCHE, A. and BOUTIN, A. M. Bull soc. chim. 31 : 546-551. 1922.
19. SMITH, D. F. and HAWK, C. O. J. Phys. Chem. 32 : 415-424. 1928.
20. STORFER, E. Z. Elektrochem. 41 : 540-541. 1935.
21. WAGNER, G., SCHWAB, G.-M., and STAEGER, R. Z. physik. Chem. 27B : 439. 1934.
22. WEISER, H. B. and MILLIGAN, W. D. J. Phys. Chem. 36 : 3010-3029. 1932.
23. WEISER, H. B. and MILLIGAN, W. D. J. Phys. Chem. 38 : 1175-1182. 1934.

Quick

Index